## REVIEW PAPER

# STRUCTURE AND RHEOLOGICAL FUNCTION OF SIDE BRANCHES OF CARBOHYDRATE POLYMERS

JAEKWAN HWANG and JOZEF L. KOKINI

*Department of Food Science*
*Rutgers University*
*P.O. Box 231*
*New Brunswick, NJ 08903*

(Manuscript received September 21, 1990; in final form January 25, 1991)

## ABSTRACT

*This review consists of two major parts: (1) the rheological theories of branched polymers and (2) the structural features of side branches of carbohydrates and their effects on the rheological properties. The rheological properties influenced by branching are discussed in terms of radius of gyration, intrinsic viscosity, zero-shear viscosity ($\eta_o$), elastic properties represented by the zero-shear recoverable compliance ($J_e^o$), shear rate dependence of viscosity, extensional viscosity and thermal sensitivity of viscosity. The second part is focused on the structural characteristics of side branches found in four typical branched carbohydrates, i.e., starch (amylopectin), galactomannan, xanthan and pectin, with an emphasis on their contribution to the rheological properties.*

## INTRODUCTION

Branching along the main backbone of synthetic polymers significantly alters rheological and other physicochemical properties (Graessley 1977; Roovers 1985a), which in turn influence the processibility of many commercial polymers (Rokudai 1979). Branches may be distributed regularly or randomly along the main backbone, or several branches may originate from a single point to generate a star-shaped molecule (Nielsen 1977). Side branches, either natural or artificial, are also found in carbohydrate polymers (Kennedy and White 1983: Yalpani 1985; Dutton 1985; Schuerch 1985; Yalpani 1987; Yalpani and Desrochers 1987). Natural side branches occur in starch (amylopectin), guar and locust bean galactomannans, pectin, acacia gum and microbial polysaccharides such as xanthan, wellan and scleroglucan gums. Side branches can be artificially incorpo-

Journal of Texture Studies **22** (1991) 123–167. *All Rights Reserved.*

rated into linear carbohydrate polymers to improve functional properties. For example, a variety of functional groups are added to linear amylose (Wurzburg 1986) and cellulose (Glicksman 1986) for the purpose of improving their functionalities.

Side branches of carbohydrates affect a variety of functional properties such as solubility, gelling, retrogradation, freeze-thaw stability, film formation and rheological properties (Dea 1987). Important functional properties of linear and branched carbohydrates are compared in Table 1. Side branches function to prevent intermolecular association of carbohydrate polymers. Thus, water molecules can penetrate more readily the intermolecular spaces caused by steric hindrance, resulting in enhancement of solubility. For the same reason the presence of side branches promotes swelling and subsequent gelatinization of carbohydrates. However, side branches inhibit the formation of junction zones required for gelling. Likewise, retrogradation of branched carbohydrates is diminished due to limited intermolecular association at low temperature, and thus branched carbohydrates are more stable for freeze-thaw treatment than linear carbohydrates. The difference between film forming properties of linear and branched carbohydrates is best illustrated by linear amylose molecules which form strong and flexible films, whereas branched amylopectin-based films are weak and brittle (Zobel 1988).

When compared to other functional properties, the significance of side branches of carbohydrate polymers in terms of affecting the rheological properties has not been systematically studied to date. This paper aims to: (1) introduce the rheological concepts relevant to branching in synthetic polymers and (2) review the structural characteristics and the rheological contribution of side branches found in carbohydrate polymers.

TABLE 1.
COMPARISON OF FUNCTIONAL PROPERTIES OF LINEAR AND BRANCHED CARBOHYDRATES

| Functions | Linear | Branched | References |
|---|---|---|---|
| Solubility | Low | High | Hui and Neukom (1964) |
| Gelatinization | Low | High | Greenwood (1979) |
| Gelling | High | Low | McCleary *et al.* (1981) |
| Retrogradation | High | Low | Wurzburg (1986) |
| Film Formation | High | Low | Zobel (1988) |
| Freeze-Thaw Stability | Low | High | Dea (1987) |
| Viscosity | High | Low | Mitchell (1979) |

## RHEOLOGY OF BRANCHED POLYMERS

Studies of branching effects are useful to understand the contribution of chain entanglements and molecular conformation to the rheological properties of polymers (Fujimoto *et al.* 1970). When polymer molecules are branched, their rheological behavior varies with the number, location and length of the branches (Graessley 1977). In this section the role of branching is discussed in terms of its effects on (1) radius of gyration and intrinsic viscosity, (2) zero-shear viscosity, (3) zero-shear recoverable compliance, (4) shear rate dependence of viscosity, (5) extensional viscosity and (6) thermal sensitivity of viscosity.

### Radius of Gyration and Intrinsic Viscosity

A linear polymer exhibits a larger hydrodynamic volume and radius of gyration relative to a branched polymer of the same molecular weight as illustrated in Fig. 1. This difference in the hydrodynamic volume affects the intrinsic viscosity. Intrinsic viscosity ($[\eta]$), radius of gyration (S) and molecular weight (M) can be related through the Flory-Fox equation (Flory 1953) as follows:

$$[\eta] = 6^{3/2}\Phi S^3/M \quad (1)$$

where the Flory constant $\phi$ is nearly a universal constant, equal to about $2.5 \times 10^{23}$ when S is given in cm and $[\eta]$ in $cm^3/g$ (Bird *et al.* 1977). Alternatively, since the root-mean-square end-to-end distance, R, is related to the radius of gyration, S, by $R = 6^{1/2}S$, Eq. 1 corresponds to $[\eta] = \phi R^3/M$ (Flory 1953). Therefore, when compared to a linear polymer, a branched polymer of the same molecular weight displays a smaller radius of gyration and correspondingly a smaller intrinsic viscosity, namely, $S_L > S_B$ and $[\eta]_L > [\eta]_B$ (Graessley 1968).

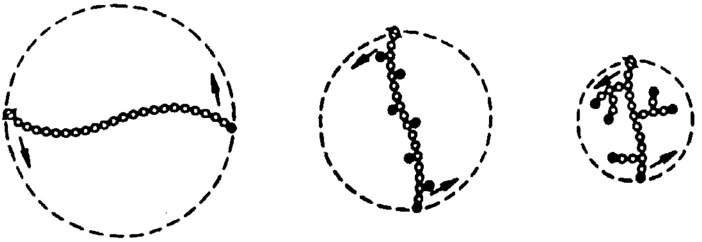

FIG. 1. SCHEMATIC REPRESENTATION OF HYDRODYNAMIC VOLUMES OCCUPIED BY LINEAR AND BRANCHED POLYMERS OF THE SAME MOLECULAR WEIGHT
*From Hodge and Osman 1976*

The branching parameter, g, was defined by Zimm and Stockmayer (1949) as the ratio of mean-square radius of gyration of a branched polymer, $S_B^2$, to that of a linear polymer, $S_L^2$, of the same molecular weight as follows:

$$g = S_B^2/S_L^2 \qquad (2)$$

From Eq. (1) and (2), the ratio of intrinsic viscosity of a branched polymer, $[\eta]_B$, to that of a linear polymer, $[\eta]_L$, of the same molecular weight can be simply related to g by

$$[\eta]_B/[\eta]_L = g^{3/2} \qquad (3)$$

Here Eq. (3) assumes a freely jointed or random-flight chain (Thurmond and Zimm 1952; Flory 1953; Graessley 1968). In reality, the freely jointed chain underestimates the true dimensions of real polymer molecules for two reasons: restrictions to completely free rotation and the excluded volume effect (Billmeyer 1984). These two factors have been counted to develop the models relating $[\eta]_B/[\eta]_L$ and g (Kim and Ree 1985). Zimm and Kilb (1959) showed

$$[\eta]_B/[\eta]_L = g^{1.0} \qquad (4)$$

neglecting hydrodynamic interactions (free draining) and entanglements of the polymer molecules in dilute solutions, which corresponds to the theory of Rouse (1953) for linear polymers. When dominant hydrodynamic interactions (nonfree draining) were taken into account in the absence of entanglements, corresponding to the theory of Zimm (1956) for linear polymers, Zimm and Kilb (1959) found

$$[\eta]_B/[\eta]_L = g^{1/2} \qquad (5)$$

It was suggested that Eq. (5) would hold for all types of branched polymers (Osaki 1973; Osaki and Schrag 1973) with some exceptions in comb-shaped polymers (Berry 1971). In general, these relations are expressed by

$$[\eta]_B/[\eta]_L = g^{\epsilon} \qquad (6)$$

where the exponent $\epsilon$ can vary from 0.5 to 1.5, depending on the theoretical assumptions employed in the model development (Small 1975; Bywater 1979).

The empirically determined $\epsilon$ values for a variety of branched polymers can be found from the report of Roovers (1985a) and Douglas *et al.* (1990).

## Zero-Shear Viscosity

The effects of branching are best established for the case of zero-shear viscosity, $\eta_o$ (Graessley *et al.* 1976). Considering hydrodynamic interactions, Bueche (1964) demonstrated that the zero-shear viscosities of a branched polymer, $\eta_{o,B}$, and a linear polymer, $\eta_{o,L}$, having the same molecular weight were relevant at the same polymer concentration by the following equation:

$$\eta_{o,B}/\eta_{o,L} = g^a \tag{7}$$

where a equals 1.0 when the molecules are not entangled, and 3.5 when the molecules are entangled. The g value is less than unity regardless of the exponent of Eq. (6), since the intrinsic viscosity of a branched polymer is smaller than that of a linear polymer of the same molecular weight, i.e., $[\eta]_B/[\eta]_L < 1.0$. Therefore, Eq. (7) indicates that $\eta_{o,B}$ is smaller than $\eta_{o,L}$, irrespective of entanglements. However, this argument is valid only at low concentration and/or low molecular weight of polymer systems, at which the branches are not significantly entangled. In this case the ratio of zero-shear viscosities, $\eta_{o,B}/\eta_{o,L}$, depends primarily on the ratio of radii of gyration, $S_B/S_L$, and thus specific details of the branching structure affect the viscosity simply through their influence on the mean coil size (Graessley 1977).

In contrast, $\eta_{o,B}/\eta_{o,L}$ begins to increase rapidly at high concentration and high molecular weight due to substantially entangled branches, and finally $\eta_{o,B}$ may overtake $\eta_{o,L}$ and then exceed it by orders of magnitude. For example, in Fig. 2A linear polyisoprene is shown to have a higher $\eta_o$ than four-arm star polyisoprene at low and intermediate concentrations ($< \approx 0.18$ g/mL), above which the opposite trend is however observed. This is because the branches are significantly entangled above the critical concentration, resulting in higher $\eta_o$ than linear polyisoprene. In contrast to four-arm star polyisoprene, six-arm star polyisoprene does not exhibit a higher $\eta_o$ than linear polyisoprene even at high concentrations studied. It is thought that significant decrease in the molecular size caused by six-arm branching becomes the predominant factor over entanglements of the branches in determining $\eta_o$. The zero-shear viscosity also follows similar trends as a function of molecular weight at the same polymer concentration as shown in Fig. 2B. These results are consistent with the reports for polybutadienes (Gruver and Kraus 1964; Kraus and Gruver 1965a, 1970) and polystyrenes (Graessley and Roovers 1979; Roovers 1984; Takahashi *et al.* 1986).

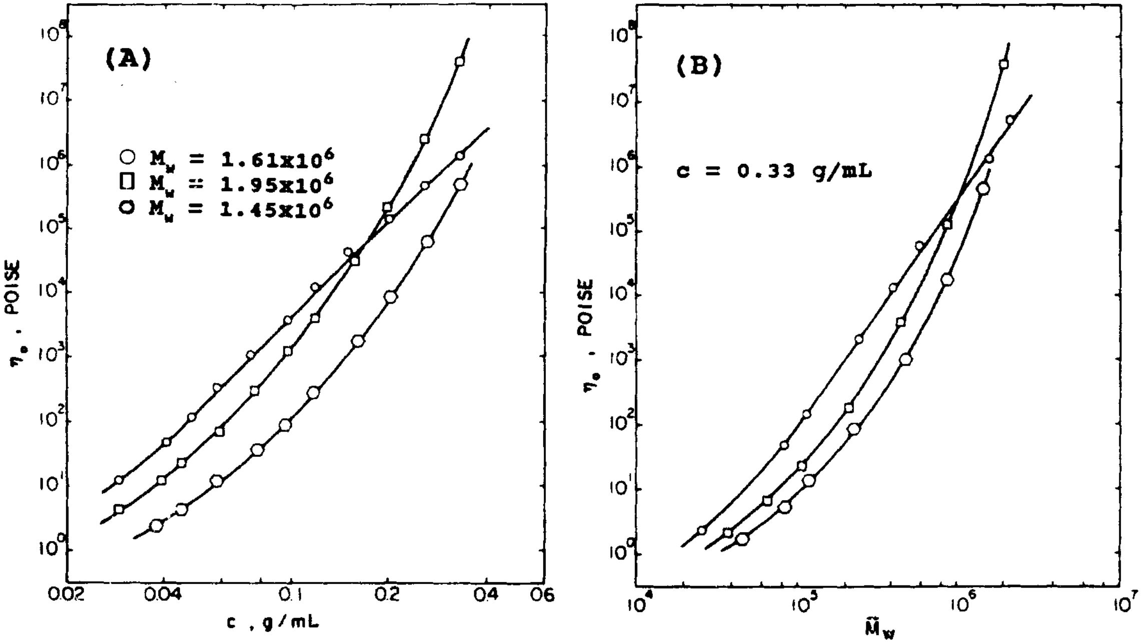

FIG. 2. ZERO-SHEAR VISCOSITY VS (A) CONCENTRATION AND (B) MOLECULAR WEIGHT OF LINEAR AND STAR-BRANCHED POLYISOPRENES

The symbols are designated as follows: ○ = Linear polymer; □ = four-arm star; ○ = six-arm star.

*From Graessley et al. 1976*

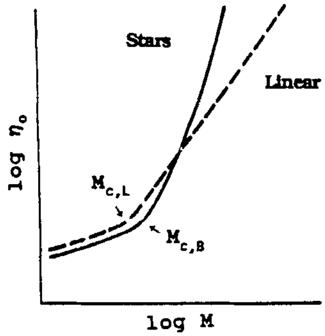

FIG. 3. ZERO-SHEAR VISCOSITY OF LINEAR AND STAR-BRANCHED POLYMERS AS A FUNCTION OF MOLECULAR WEIGHT
*From Graessley 1984*

The generalized $\eta_o$ vs $M_w$ curve for linear and star-branched polymers can be separated into two regions by a characteristic molecular weight, $M_c$, as presented in Fig. 3. The polymer molecules are significantly entangled at $M_w > M_c$, leading to a sudden increase in $\eta_o$ (Berry and Fox 1968; Graessley 1974, 1982a). It is observed that for linear polymers

$$\eta_{o,L} \propto M_w \qquad \text{at } M_w < M_{c,L} \tag{8}$$

and

$$\eta_{o,L} \propto M_w^{3.4} \qquad \text{at } M_w > M_{c,L} \tag{9}$$

where $M_w$ is the weight average molecular weight (Nielsen 1977; Valles and Macosko 1979). $\eta_{o,B}$ also conforms to the same order as that of linear polymers at $M_w < M_{c,B}$. On the other hand, the order of $\eta_{o,B}$ varies depending on entanglements of the branches at $M_w > M_{c,B}$, which is in contrast to linear polymers obeying the 3.4 power law. Considering the enhancement effect of entangled branches on $\eta_{o,B}$, Eq. (7) can be modified for f-arm star polymers as follows (Graessley 1977, 1982b; Roovers 1984):

$$\eta_{o,B} = g^a\ \eta_{o,L} \exp[\alpha(2M/fM_c)] \tag{10}$$

and

$$g = (3f-2)/f^2 \tag{11}$$

where g is the branching parameter defined in Eq. (2), a is a constant depending on polymer entanglements as shown in Eq. (7), $\alpha$ is a constant, and f is the number of arms. Eq. (10) becomes $\eta_{o,B} = g\ \eta_{o,L}$ at $2M < fM_c$ due to the negligible exponential term (Roovers 1984). Accordingly, $\eta_{o,B}$ is always lower than $\eta_{o,L}$ of the same molecular weight, since g is less than unity. In this case the molecular size in terms of radius of gyration and intrinsic viscosity governs the overall $\eta_o$. In contrast, Eq. (10) becomes $\eta_{o,B} = g^{3.5}\ \eta_{o,L} \exp[\alpha(2M/fM_c)]$ when $2M > fM_c$ (Roovers 1984). Thus, $\eta_{o,B}$ begins to increase exponentially and can exceed $\eta_{o,L}$ at fairly high molecular weights, i.e., $2M >> fM_c$. The degree of branching can affect the critical molecular weight above which $\eta_{o,B}$ is greater than $\eta_{o,L}$: the higher branching, the higher critical molecular weight due to its decreasing effect on g in Eq. (10). An example can be found in Fig. 2B where $\eta_o$ os six-star polybutadiene seemingly overtakes $\eta_o$ of linear polybutadiene at the higher molecular weight than that of four-star polybutadiene. Therefore, these arguments indicate that whether or not $\eta_{o,B}$ is greater than $\eta_{o,L}$ is a compromise between the molecular size determined by the degree of branching and the entanglements of branches. Figure 3 also implies that $M_c$ of linear polymers is less than that of branched polymers of the same molecular weight, i.e., $M_{c,L} < M_{c,B}$, which is consistent with the report of Nielsen (1977). This is because linear polymers have greater propensity to be entangled with other polymer molecules because of their larger molecular size than branched polymers of the same molecular weight. Both concentration and molecular weight should be considered together to understand entanglements of the polymer molecules. For example, although molecular weight of a branched polymer is fairly high, $\eta_{o,B}$ will not exceed $\eta_{o,L}$ of the same molecular weight in dilute solutions due to insignificant entanglements of the branches. Thus, the product of concentration and molecular weight, cM, can be a good parameter in terms of evaluating entanglements of the polymer molecules. $\eta_o$ vs cM can be divided into two distinct regions at $cM = (cM)_c$, above which the polymer molecules are significantly entangled (Graessley 1974). When the product cM is low, branched polymers display lower $\eta_o$ than linear polymers, and vice versa at high cM (Roovers 1981). In practice, the critical cM point in the entangled region, above which $\eta_{o,B}$ is greater than $\eta_{o,L}$, is empirically determined.

The concentration where entanglements of the branches begin to appear depends on the branching structure of polymers and particularly on the length of the branches (Graessley 1977). Short branches generally do not affect the viscosity of polymer melts, rather influencing the morphology and solid-state properties of semicrystalline polymers, whereas long branches can have a remarkable effect on solution viscosity and melt rheology (Nielsen 1977; Nordmeier *et al.* 1990). Branches which are long, but which are still shorter than those required for entanglements decrease the viscosity when compared to a linear polymer of the same molecular weight (Miltz and Ram 1973; Utracki and Roovers 1973). This is because the polymer molecules containing such branches are more compact than the linear molecules of the same molecular weight, leading to smaller molecular size. However, if the branches are so long that they can participate in entanglements, branched polymers may have greater viscosity than linear polymers of the same molecular weight (Kraus and Gruver 1965b; Graessley 1977).

Here Eq. (10) can be modified in terms of the molecular weight of an arm, $M_a$, to clearly understand the effects of the branch length. For f-arm star polymers with the equal length

$$M_a = M/f \tag{12}$$

In addition, Graessley (1977, 1984) showed that $M_c$ approximated twice the molecular weight between entanglements, $M_e$, i.e.,

$$M_c \approx 2\ M_e \tag{13}$$

From Eq. (10), (12) and (13)

$$\eta_{o,B} = g^a\ \eta_{o,L}\ \exp[\alpha(M_a/M_e)] \tag{14}$$

The constant $\alpha$ can be obtained from the slope of $J_e^o G_N^o$ vs $(M_a/M_e)$ or the logarithmic plot of $\eta_o(M_a/M_e)^{-1/2}$ vs $(M_a/M_e)$, where $G_N^o$ is the plateau modulus (Pearson and Helfand 1984). In the case of short branches or $M_a < M_e$, the exponential term of Eq. (14) is negligible, and $\eta_{o,B}$ is less than $\eta_{o,L}$ due to $g < 1.0$. When $M_a >> M_e$ or the branches are long enough to be highly entangled, $\eta_{o,B}$ increases exponentially with the branch length or equivalently with the number of entanglements per branch (Berry and Fox 1968; Roovers 1985a) and finally overtakes $\eta_{o,L}$. Typically when $M_a$ exceeds 2–4 times $M_c$, $\eta_{o,B}$ begins to increase rapidly (Graessley 1984). This exponential dependence of $\eta_{o,B}$ on the branch length can be found elsewhere (Doi and Kuzuu 1980; Graessley 1982b; Roovers 1985a, b; McLeish 1988). The relation $\eta_{o,B} > \eta_{o,L}$ in highly entangled polymer systems was observed in all types of branched polymers, namely, star- (Graessley *et al.* 1976; Graessley and Roovers 1979), comb- (Fujimoto *et al.* 1970; Roovers and Graessley 1981) and random-branched polymers (Graessley and Shinbach 1974; Münstedt and Laun 1981). Especially, in the case of comb-shaped polymers, the enhancement of $\eta_{o,B}$ can be influenced not only by the branch length but also by the spacing of branching along the main backbone (Roovers and Graessley 1981). Unfortunately, a complete theory for the melt behavior of comb- and random-branched polymers has not yet been developed. It should be recognized that the enhancement effect of long branches on $\eta_o$ decreases rapidly as the polymer is diluted, and eventually the viscosity returns to the dependence on the molecular size alone (Graessley 1984). The exponential dependence of the longest relaxation time on the branch length was reported by Roovers and Toporowski (1987).

## Zero-Shear Recoverable Compliance

The zero-shear recoverable compliance, $J_e^o$, has long been considered as a useful parameter of fluid elasticity (Han 1976). $J_e^o$ characterizes the elastic coil that occurs when the external forces producing the steady-state flow are suddenly removed (Graessley 1977). Neglecting hydrodynamic interactions and entanglements of the linear polymer molecules, Rouse (1953) theoretically predicted $J_e^o$ of linear polymers as follows:

$$J_e^o = 0.4\ M/cRT \qquad (15)$$

where c is the polymer concentration, M is the molecular weight, R is the gas constant, and T is the absolute temperature. This was modified by Ham (1957) for star-branched polymers with arms of the equal length as follows:

$$J_e^o = 0.4\ g_2\ M/cRT \qquad (16)$$

and

$$g_2 = (15f-14)/(3f-2)^2 \qquad (17)$$

where f is defined as the number of arms emanating from the same junction point, and a linear polymer gives $f = 1.0$. Equation (17) indicates that $g_2$ is unity for a linear polymer and becomes less than unity with increasing the number of arms. It can be seen from Eq. (15) and (16) that $J_e^o$ of linear polymers is higher than that of branched polymers of the same molecular weight. Ham (1957) obtained the terminal relaxation time ($\tau_1$), $\eta_o$, and $J_e^o$ of star-branched polymers with arms of the unequal length in relation to a linear polymer of the same molecular weight in dilute solutions. The results are presented in Table 2. $\tau_1$, $\eta_o$ and $J_e^o$ of the branched molecules are always smaller than those of the linear

TABLE 2.
COMPARISON OF $\tau_1$, $\eta_0$ and $J_e^o$ FOR LINEAR AND STAR-BRANCHED POLYMERS OF THE SAME MOLECULAR WEIGHT IN DILUTE SOLUTIONS

| Lengths of Branches* | $\tau_{1,B}/\tau_{1,L}$ | $\eta_{o,B}/\eta_{o,L}$ | $J^o_{e,B}/J^o_{e,L}$ |
|---|---|---|---|
| 1/4, 1/4, 1/2 | 0.68 | 0.81 | 0.76 |
| 1/5, 1/5, 3/5 | 0.80 | 0.86 | 0.89 |
| 1/5, 2/5, 2/5 | 0.64 | 0.81 | 0.73 |
| 1/4, 1/4, 1/4, 1/4 | 0.25 | 0.63 | 0.46 |
| 1/5, 1/5, 1/5, 2/5 | 0.48 | 0.66 | 0.60 |
| 1/6, 1/6, 1/3, 1/3 | 0.60 | 0.67 | 0.58 |
| 1/5, 1/5, 1/5, 1/5, 1/5 | 0.16 | 0.52 | 0.36 |
| 1/6, 1/6, 1/6, 1/6, 1/3 | 0.48 | 0.56 | 0.49 |

Source: Ferry (1980).
*The ratios of the length of each branching to that of a linear polymer having the same molecular weight.

molecule in dilute solutions, irrespective of the branching distribution. The larger the number of branches and the more nearly equal their length, the greater the discrepancy. It is also found that $\tau_1$ is the most sensitive of the three quantities. As discussed earlier for $\eta_o$, the relation $J_{e,L}^o > J_{e,B}^o$ holds for the polymer system that there is no substantial participation in entanglements of the branches. This trend can be reversed with significant coupling entanglements of the branches (Ferry 1980). Examples showing $J_{e,B}^o > J_{e,L}^o$ in the entangle system can be found in star- (Masuda *et al.* 1971, 1981; Graessley *et al.* 1976; Graessely 1977; Graessley and Roovers 1979; Raju *et al.* 1981; Masuda *et al.* 1984), comb- (Fujimoto *et al.* 1970; Roovers and Graessley 1981) and random-branched polymers (Valentine *et al.* 1968; Jacovic *et al.* 1979).

The molecular weight dependence of $J_e^o$ is schematically shown for linear and star-branched polymers in Fig. 4. $J_e^o$ of linear polymers is directly proportional to molecular weight at low molecular weight and becomes independent of molecular weight at high molecular weight. The two regions are separated by another characteristic molecular weight, $M'_c$. Experimentally, Graessley (1974) showed that $M'_c$ of linear polymers approximated $7M_e$, which is in fairly good agreement with the theoretical value, $7.2M_e$, of Doi (1981). Considering both concentration and molecular weight, Graessley (1974, 1982a) and Roovers (1981) demonstrated that for linear polymers $J_e^o \propto c^{-1}M^1$ at $cM < (cM)'_c$ and $J_e^o \propto c^{-2}M^0$ at $cM > (cM)'_c$. Here $(cM)'_c$ is the intersection point of $J_e^o$ vs. cM. On the other hand, $J_e^o$ of branched polymers is consistently increased with molecular weight, i.e., $J_e^o \propto c^{-1}M^1$. Therefore, $J_e^o$ of branched polymers is lower than that of linear polymers at low molecular weight because of $g_2 < 1.0$, but the reverse becomes true at high molecular weight.

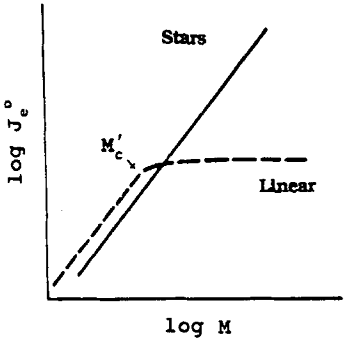

FIG. 4. ZERO-SHEAR RECOVERABLE COMPLIANCE OF LINEAR AND STAR-BRANCHED POLYMERS AS A FUNCTION OF MOLECULAR WEIGHT
*From Graessley 1984*

The creep compliance, $J_c$, is experimentally determined by measuring the first normal stress difference as a function of shear rate (Bird *et al.* 1977; Han 1976):

$$J_e = (\tau_{11} - \tau_{22})/2\tau^2 \qquad (18)$$

or

$$J_e = \Psi_1/2\eta^2 \qquad (19)$$

16

where $\tau_{11} - \tau_{22}$ is the first normal stress difference, $\tau$ is the shear stress, $\psi_1$ is the primary first normal stress coefficient ($\psi_1 = (\tau_{11} - \tau_{22})/\dot{\gamma}^2$), and $\eta$ is the steady shear viscosity ($\eta = \tau/\dot{\gamma}$). Here $J_e^\circ$ can be estimated at the low shear rate as follows (Graessley 1974; Ferry 1980):

$$J_e^\circ = \lim_{\dot{\gamma} \to 0} (\tau_{11} - \tau_{22})/2\eta_0^2\dot{\gamma}^2 \qquad (20)$$

This represents how the first normal stress difference, $(\tau_{11} - \tau_{22})$, is related to $J_e^\circ$ of a polymeric system. Figure 5 shows that branched low-density polyethylene (LDPE) exhibits the higher first normal stress difference than linear high-density polyethylene (HDPE). These results suggest that branched polymers confer more elasticity as compared to linear polymers (Han 1976).

The remarkable increase of $\eta_0$ and $J_e^\circ$ due to branching above certain concentration and molecular weight can be understood most satisfactorily within the framework of the polymer tube and reptation model introduced by De Gennes (1971), who demonstrated the mobility of flexible linear chains in a network

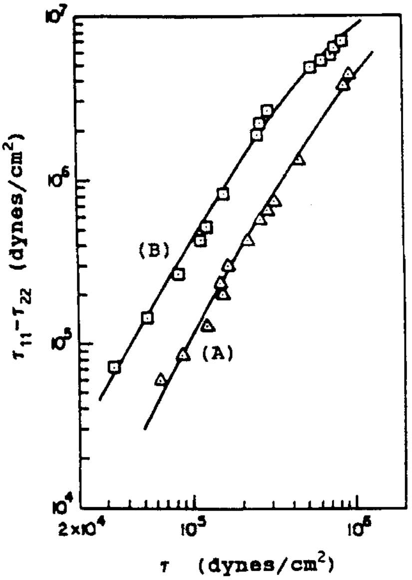

FIG. 5. FIRST NORMAL STRESS DIFFERENCE VS SHEAR STRESS OF POLYETHYLENES (A) HDPE, $M_w/M_n = 16$, $M_n = 1.4 \times 10^4$; (B) LDPE, $M_w/M_n = 20$, $M_n = 2.0 \times 10^4$
*From Han 1976*

filled with loop-like obstacles. As illustrated in Fig. 6, in concentrated solutions a polymer molecule is filled with other polymer molecules and forms uncrossable entanglements which act as a barrier, thus reducing mobility (Graessley 1982a). The polymer chain lies within a tunnel among the obstacles, defined by its own contour as shown in Fig. 7A. The obstacles prevent transverse or lateral motions,

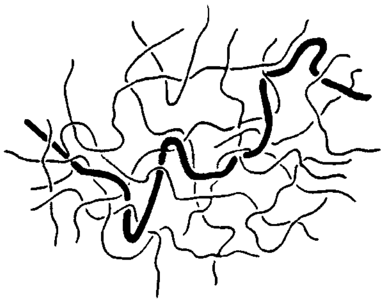

FIG. 6. A POLYMER CHAIN AND ITS SURROUNDINGS IN AN ENTANGLED POLYMER LIQUID
*From Graessley 1982a*

so that the polymer chain must wind its way along its tunnel by small Brownian displacements, continually creating a new tunnel as it moves out among new obstacles (Graessley 1977; Larson 1988). This indicates that the primary mode of relaxation is a simple snake-like diffusion of the polymer along a path approximately following its contours (Pearson and Helfand 1983). This snake-like motion was termed reptation (De Gennes 1971). Later, Doi and Edwards (1978) extended this reptation idea to develop theories predicting chain dynamics and viscoelastic behavior of the entangled linear polymer molecules.

For branched polymers, the movement of the polymer molecules would be prevented or at least drastically suppressed, since the branched chain is effectively pinned in its tunnel of obstacles at the branched point as shown in Fig. 7B. Therefore, branching must greatly reduce the translational diffusion coefficient, and the macroscopic viscosity is correspondingly increased (Graessley *et al.* 1976; Klein *et al.* 1983; Fleischer 1985; Graessley 1984; Klein 1986). The pin is released only if a free end retraces its tunnel back to the branching point. In this situation, displacements can still occur but only until the next pinning obstacle is met, requiring a new unthreading. Mobility is thus controlled by the unthreading rate, which in turn depends on the number of obstacles or entanglements along the branches. Accordingly, any branch point should reduce mobility if at least three strands emanating from it are each long enough to participate in several entanglements (Graessley 1977). Restricted reptation of branched polymers in concentrated solutions could not be expected to significantly occur at

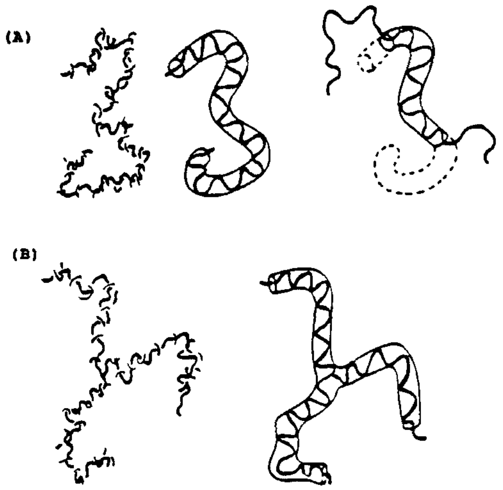

FIG. 7. ILLUSTRATION OF THE CONSTRAINING EFFECTS OF CHAIN-LIKE SURROUNDINGS FOR (A) LINEAR AND (B) BRANCHED MOLECULES
*From Graessley 1982b*

low concentration and/or low molecular weight of polymer systems. Since the hydrodynamic molecular size occupied by a polymer molecule determines viscoelastic properties, branched polymers should exhibit smaller $\eta_o$ and $J_e^o$ than linear polymers of the same molecular weight. These results can be reversed in entangled or concentrated polymer systems, in which restricted reptation of the branched polymer molecules plays an important role in enhancing $\eta_o$ and $J_e^o$ (Graessley 1977; Ferry 1980).

## Shear Rate Dependence of Viscosity

The branching effect on viscosity versus shear rate behavior is illustrated in Fig. 8, where the shear viscosity of a branched polymer is higher than that of a linear polymer at low shear rates, and vice versa at high shear rates. These observations can be interpreted in terms of different disentangling response of linear and branched polymers to the shear force. Entanglements might be considered as the weakly linked noncovalent crosslinks, which are readily reversible when the shear force is exerted. In contrast to linear polymers having only main chain entanglements, branched polymers can be entangled through the branches as well as the main chains (Fujimoto *et al.* 1970). Therefore, the results shown in Fig. 8 indicate that branch-associated entanglements are more sensitive to the shear force than main chain entanglements. This is in good agreement with the report of Jacovic *et al.* (1979) and Graessley (1984). Significant entanglements of the branches can account for the higher viscosity of branched polymers at low shear rates. This trend is reversed at high shear rates, at which hydrodynamic size of polymers determines the overall shear viscosity. In summary, the viscosity of branched polymers is more shear rate dependent than that of linear polymers.

Shear rate dependence of the viscosity can be estimated quantitatively by using dimensionless rheological parameters. Graessley *et al.* (1976) demonstrated that

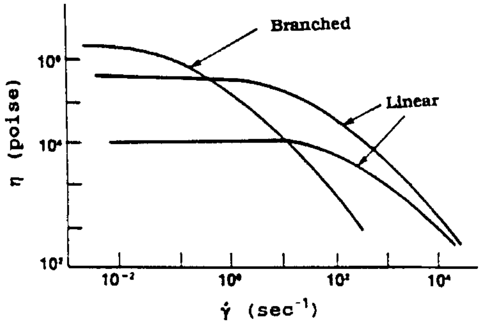

FIG. 8. SHEAR RATE DEPENDENCE OF THE VISCOSITY OF LINEAR AND BRANCHED POLYMERS
*From Graessley 1984*

the product $\eta_o J_e^o \dot{\gamma}_o$ was essentially the same for all polyisoprene samples, independent of concentration, molecular weight and branching. The generalized relation was described for steady and dynamic rheological measurements by Roovers (1985a) as follows:

$$\eta_o J_e^o \dot{\gamma}_o \approx \eta_o J_e^o \omega_o \approx 0.6 \tag{21}$$

where $\eta_o$ is the zero-shear viscosity, $J_e^o$ is the zero-shear recoverable compliance, $\dot{\gamma}_o$ and $\omega_o$ are the shear rate (1/s) and the frequency (rad/s), respectively, at which $\eta = 0.8\eta_o$. Since $\eta_o$ and $J_e^o$ of branched polymers are higher as described previously, $\dot{\gamma}_o$ and $\omega_o$ of branched polymers are lower than those of linear polymers. This reflects that the onset of non-Newtonian flow of branched polymers occurs at lower shear rates than linear polymers as shown in Fig. 8. This high sensitivity of branching to shearing explains why branched polymers initially displaying higher zero-shear viscosity may have lower viscosity at high shear rates than linear polymers (Roovers 1985a).

## Extensional Viscosity

The response of linear and branched polymers to shear and extensional or elongational forces are illustrated in Fig. 9. The shear force gives both deformation and rotation, whereas the normal extensional force results in only deformation without rotation (Darby 1976; Samurkas *et al.* 1989). In shear flow the overall shape of the viscosity curve is similar for linear and branched polymers, although the absolute magnitude of shear viscosity and its dependence on shear rates are somewhat different as presented in Fig. 8. When the molecules are highly ordered by extensional (stretching) flow, the branching points can act

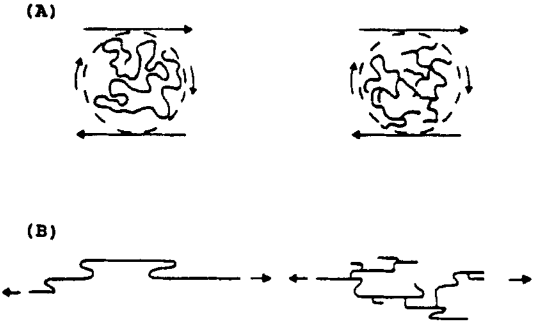

FIG. 9. SCHEMATIC DIAGRAM OF (A) SHEAR AND (B) EXTENSIONAL FLOWS OF LINEAR AND BRANCHED POLYMERS
*From Cogswell 1981*

as hooks, resulting in increasing the resistance to flow. Therefore, while linear polymers thin down under extensional forces, branched polymers tend to stiffen or "strain harden". Thus, polymer melts which are superficially similar in other rheological tests may be remarkably different in thier extensional flow behavior (Cogswell 1981; Barnes *et al.* 1989). The use of only steady-state viscosity appears to be sufficient in most cases of extrusion and injection molding processing, whereas the elongational properties of polymer melts becomes relevant for processing such as converging flow, fiber spinning, tubular film blowing and blow molding (Han 1976; Laun and Schuch 1989).

"Strain hardening" is typically observed in LDPE having random tree-like branches (Laun and Münstedt 1976, 1978; Münstedt and Laun 1981; Soskey and Winter 1985). Münstedt and Laun (1981) investigated extensional viscosities of three polyethylenes having different degrees of branching. The results are shown in Fig. 10. It is observed that the magnitude of extensional viscosity is proportional to the degree of branching. This is consistent with the report of Minoshima and White (1986a) and Laun and Schuch (1989). In contrast, Au-Yeung *et al.* (1981) observed that hydrogenated polybutadiene having star-shaped long branches did not exhibit elongational stretching phenomena. These results indicate that both the extent and the structural features of branching might be crucial in determining the elongational rheology. In practice, strain hardening

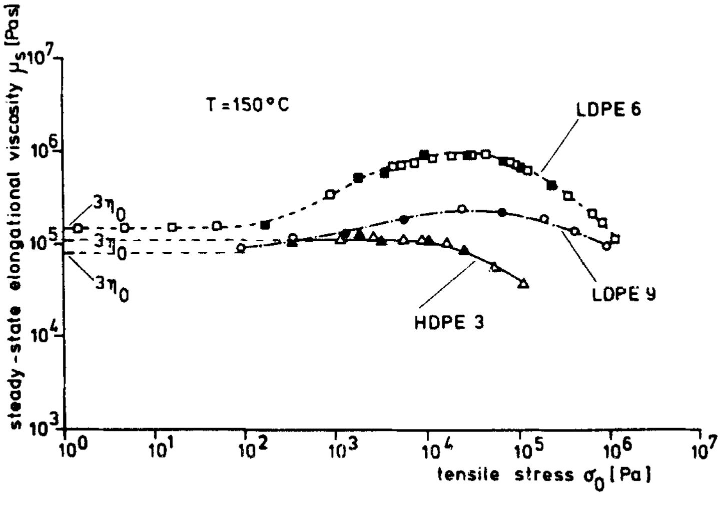

FIG. 10. STEADY-STATE ELONGATIONAL VISCOSITIES OF 3 POLYETHYLENES WITH DIFFERENT DEGREES OF BRANCHING

The number of $Ch_3$-end groups per 1000 $CH_2$ of HDPE 3, LDPE 9 and LDPE 6 are 0, 15 and 30, respectively.

*From Münstedt and Laun 1981*

of branched LDPE is important in the film blowing processing, since it gives the superior bubble stability when compared to linear HDPE of comparable molecular weight (Cogswell 1981; Münstedt 1981; Minoshima and White 1986b).

In addition, extensional flow properties are closely related to the development of vortices in the entry region (Cogswell 1972; Ma *et al.* 1985; White and Baird 1986; White *et al.* 1987). As stated above, branching of the polymer is a significant contributor to the extensional viscosity. It is conceivable that branching plays a critical role in the occurrence of vortices.

## Thermal Sensitivity of Viscosity

Branching also affects the temperature dependence of viscosity. Cogswell (1981) compared the temperature dependence of LDPE, HDPE and polypropylene (PP) by the ratio of the viscosities at 190°C to at 230°C. Here PP can be considered a polymer containing short side chains ($-CH_3$) with the same main backbone as LDPE. It was reported that the viscosity ratios ($\eta_{190}/\eta_{230}$) of branched LDPE, linear HDPE and PP were 2.9, 2.1 and 2.1, respectively. The branching structure of LDPE contributes to the more sensitive response of the viscosity to temperature than HDPE. It is also noted that short side chains do not affect thermal sensitivity, since linear HDPE and short branched ($-CH_3$) PP exhibit the same viscosity ratios. This is consistent with the observation of Porter *et al.* (1968), who reported that short branches consisting of single or two $CH_2$ groups did not contribute significantly to thermal sensitivity of the viscosity of polyethylene.

Jacovic *et al.* (1979) measured the apparent viscosity of HDPE, LDPE and its blendings as a function of stress at two different temperatures, 150° and 190°C. Then, the flow activation energy ($E_\tau$) at constant stress was calculated by the following equation:

$$E_\tau = 2.303 R (\log \eta_{150} - \log \eta_{190})/(1/423 - 1/463) \qquad (22)$$

where R is the gas constant, $\eta_{150}$ is the apparent viscosity at 150°C, and $\eta_{190}$ is the apparent viscosity at 190°C. $E_\tau$ calculated by Eq. (22) is plotted as a function of shear stress in Fig. 11. The flow activation energy of LDPE with long branches is high and decreases with increasing stress, which is in contrast to the low and almost constant value of HDPE. With increasing stress, entanglements between main chain and side branches are reduced as manifested in a viscosity decrease. Accordingly, long-branch disentanglements are apparently more sensitive to changes in the shear force, i.e., lowering $E_\tau$ with increasing $\tau$. Considering $E_\tau$ as a temperature coefficient of viscosity, long-branch entanglements are shown

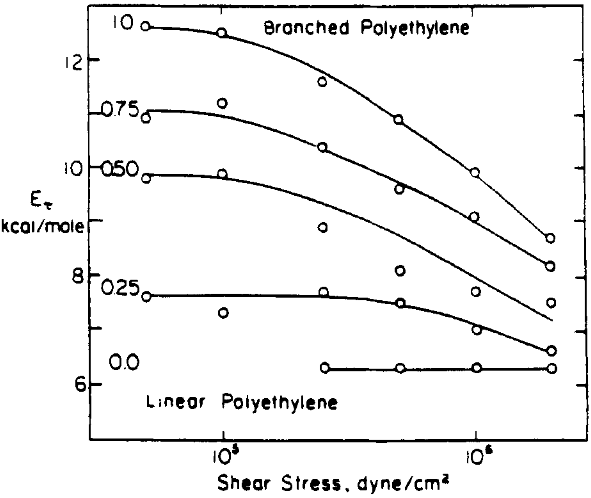

FIG. 11. FLOW ACTIVATION ENERGY OF HDPE, LDPE AND THEIR BLENDINGS AS A FUNCTION OF SHEAR STRESS
Numbers represent the weight ratios of LDPE to HDPE.
*From Jacovic et al. 1979*

to be more temperature sensitive than main chain entanglements (Jacovic *et al.* 1979). These results are in good agreement with the observations of Raju *et al.* (1979), Graessley (1977, 1982b) and Graessley and Raju (1984).

## STRUCTURE OF SIDE BRANCHES OF CARBOHYDRATES AND THEIR ROLE ON THE RHEOLOGICAL PROPERTIES

Although polysaccharides are frequently and widely utilized to improve the rheological properties in food systems as thickening and stabilizing agents, the contribution of side branches of carbohydrate polymers to the rheological properties has not attracted as much interest as synthetic polymers. This is mainly because side branches of carbohydrates are not of significant molecular length, with the exception of pectins and starch. Other functional properties such as solubility and intermolecular associated phenomena, i.e., gelling, retrogradation, freeze-thaw stability and film formation, have been extensively investigated, since they can be substantially affected by the presence of short side branches. In this section the structural features (chemical composition and distribution) of some carbohydrates containing natural side branches, i.e., starch, galactomannan, xanthan and pectin are discussed in conjunction with their contribution to the rheological properties.

## Starch

Starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-D-(1,4) glycosidic bonds (Wurzburg 1986). Starch occurs in the form of water-insoluble roughly spherical granules ranging in size from 2–100 μm, and the shape and size distribution of the granules are characteristic of the particular plant species (Banks and Muir 1980). The starch granule can be separated into two distinctly different components, amylose and amylopectin, which vary in relative amount among sources from less than 2% amylose in waxy maize to about 80% amylose in amylomaize, but the majority of starches contain between 15% and 35% amylose (Kennedy and White 1983).

Amylose is essentially a linear polymer in which the anhydroglucose units are linked through α-D-(1,4) glycosidic bonds (Hodge and Osman 1976; Whistler and Daniel 1985). Amylose is found with molecular weights ranging from $10^5$–$10^6$, corresponding to degrees of polymerization (DP) ranging approximately from 500–5000 (Galliard and Bowler 1987). Its molecular size varies depending on the plant sources and the processing conditions employed in extracting the starch.

Amylopectin is a highly branched polymer containing, in addition to anhydroglucose units linked together as in amylose through α-D-(1,4) glycosidic bonds, branches linked by α-D-(1,6) glycosidic bonds at the C-6 position (Hodge and Osman 1976; Whistler and Daniel 1985). Robin *et al.* (1974) proposed a amylopectin model based on the cluster structure as shown in Fig. 12. This cluster model is in accord with the relatively high viscosity of amylopectin compared to glycogen which has a higher molecular weight, the crystallinity as revealed by X-ray analysis and the relative resistance of parts of the molecule to attack by acid and amylolytic enzymes (Manners 1989). The A chains are joined to the remainder of the amylopectin molecule with a single α-(1,6) bond through the reducing end group. The B chains are also linked through α-(1,6) bond as the A chains, but may carry one or more A and/or B chains. The single C chain is not substituted at its reducing end group designated by ϕ in Fig. 12, and thus there is only one C chain in a amylopectin molecule. The A and B chains are linear and have an approximate degree of polymerization (DP) of 15 and 45, respectively. The associated clusters of A chains are primarily responsible for the crystalline regions within the granule. The intercrystalline amorphous areas occurring at 60–70 Å intervals contain the majority of the α-(1,6) linkages and are relatively susceptible to hydrolytic agents such as various enzymes and acids (French 1984). Overall, the amylopectin molecule is 100–150 Å in diameter and 1200–4000 Å long (French 1984). Within the granule, amylose may be located between amylopectin molecules and may be associated with the linear regions of the amylopectin molecule. Such an arrangement contributes to the high degree of order in the crystalline regions of the amylopectin (Hood 1982).

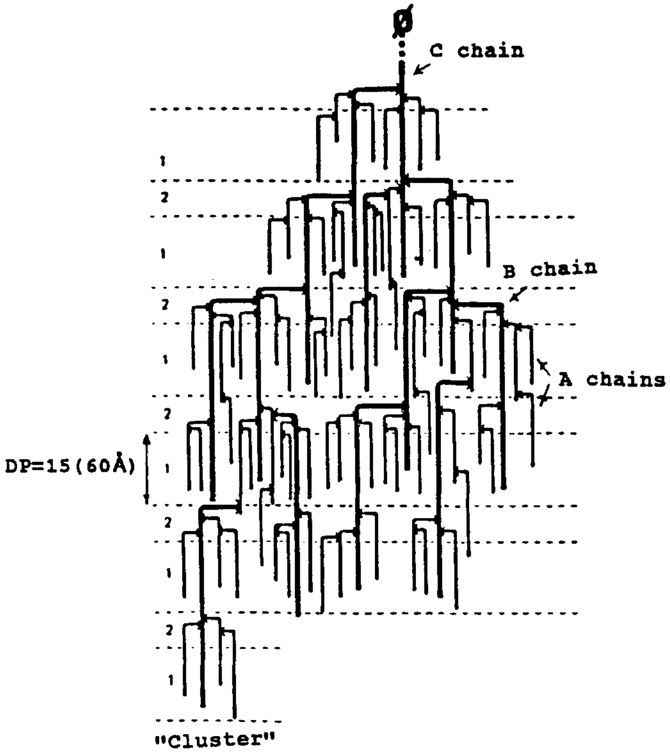

FIG. 12. STRUCTURE OF AMYLOPECTIN
1 = Crystalline region; 2 = Amorphous region; → = α-(1,6) Branching points.
*From Robin et al. 1974*

Heterogeneity in branching of amylopectin was investigated in detail by Thurn and Burchard (1985). Technically, size exclusion chromatography (SEC) and on-line low-angle laser light scattering (LALLS) system can be successfully employed to characterize the branching structure of amylopectin (Burchard 1983; Yu and Rollings 1987, 1988).

Side branches of amylopectin are not significantly distinguishable from the main backbone in terms of length and composition. This is in contrast to other branched carbohydrates which posses a long main backbone and short side substituents with different chemical composition from the main backbone. The structural details of other branched carbohydrates will be discussed later. Rheological parameters of amylose and amylopectin at the same molecular weight are not available due to significantly different molecular weights. Mitchell (1979) reported that amylopectin (Mw = 90,000,000) and amylose (Mw = 1,750,000) exhibited 127 and 154 mL/g of intrinsic viscosities, respectively. It is noted that amylose with a molecular weight approximately 50 times smaller than amylopectin displays higher intrinsic viscosity. This can be ascribed to the bushed-shaped and thereby very compact structure of amylopectin as presented in Fig. 12. The low intrinsic viscosity of amylopectin is consistent with Graessley's (1968) arguments suggesting that a branched polymer should have a smaller intrinsic viscosity relative to a linear polymer.

Greenwood (1979) studied the viscosity changes of three genotypes of maize starch, i.e., normal maize, waxy maize containing less than 2% amylose and amylomaize containing more than 80% amylose (Kennedy and White 1983) during gelatinization and subsequent cooling. Waxy maize starch showed the lower viscosity as compared to normal maize starch. This can be attributed to the fact that the radius of gyration of the branched amylopectin-based waxy starch is smaller due to its more compact conformation (Mitchell 1979), and the presence of side branches of waxy starch prevents intermolecular association and thus remains in solution during cooling (Wurzburg 1986). In contrast, normal maize starch produces junction zones through intermolecular association of the linear amylose molecule during cooling, resulting in significant viscosity increase due to gel formation (Smith 1982; Morris 1990). The initial rapid increase in viscosity was observed for waxy maize starch due to its high swellability caused by the presence of side branches. Amylomaize starch consisting mostly of amylose content did not display any viscosity development due to the lack of swellability (Greenwood 1979). In summary, the branching structure of amylopectin promotes swelling and subsequent gelatinization during the heating stage, and it prevents gelation induced by intermolecular association during the cooling stage.

## Galactomannan

Galactomannans are polysaccharides consisting of a β-(1,4)-linked linear D-mannan backbone with variable side chain substitutions of a single α-(1,6)-linked D-galactopyranosyl unit (Glicksman 1986). Figure 13 shows that the approximate galactose:mannose (G/M) ratios of 3 commercial galactomannans are 1:4 for locust (carob) bean gum, 1:3 for tara gum, and 1:2 for guar gum (Neukom 1989).

Three different distribution patterns of the galactose substituents have been proposed, i.e., uniform, block and random distribution (McCleary and Neukom 1982). Palmer and Ballantyne (1950) and Baker and Whistler (1975) proposed models suggesting that the galactose residues of guar galactomannan were alternatingly distributed along the mannan backbone in a uniform fashion. A block-type distribution of the galactose residues was suggested by Dea *et al.* (1972), Child and Pryce (1972), Painter *et al.* (1979) and Hall and Yalpani (1980). This model indicates that the galactose residues are clustered in blocks among the

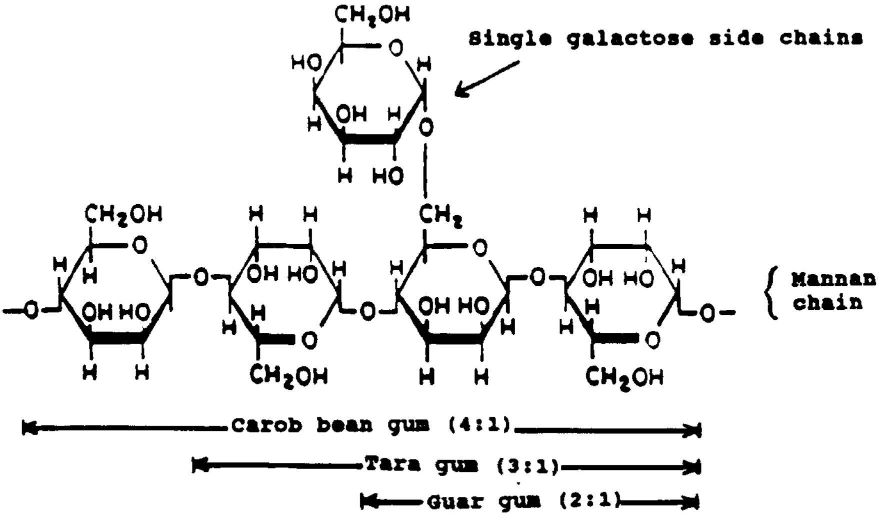

FIG. 13. STRUCTURE OF 3 GALACTOMANNANS
*From Neukom 1989*

mannan backbone, thus exhibiting the alternative sequences of "smooth" regions consisting of unsubstituted mannose residues and "hairy" regions substituted with the galactose residues. However, studies based on NMR (Grasdalen and Painter 1980; Gupta and Grasdalen 1989; Smirnova and Shcherbukhin 1989), enzymatic degradation of the mannan backbone by purified β-mannase (McCleary 1979; McCleary *et al.* 1984a, 1985) and X-ray diffraction (Marchessault *et al.* 1979; Winter *et al.* 1984) suggest an irregular to random distribution of the galactose residues of galactomannans. Consequently, the compositional ratios of galactomannans shown in Fig. 13 only display a statistical view, since galactose substituents are not distributed uniformly among the mannan chain backbone.

McCleary *et al.* (1981) reported that the removal of the galactose residues using α-D-galactosidase devoid of β-D-mannase did not affect significantly the specific viscosity of locust bean and guar galactomannans in dilute solutions ($c < c^*$) as shown in Fig. 14. The eventual viscosity decrease observed was attributed to the formation of insoluble precipitate by the association of D-mannan backbone. Fig. 15A shows the intrinsic viscosity curves of galactomannan samples containing a variety of the G/M ratios. The removal of galactose from guar galactomannan increases the intrinsic viscosity and the slope of viscosity curves. This is also consistent with the earlier discussion suggesting that the intrinsic viscosity of the linear molecular would be larger than that of the corresponding branched polymer. When the viscosity curves are plotted against the concentra-

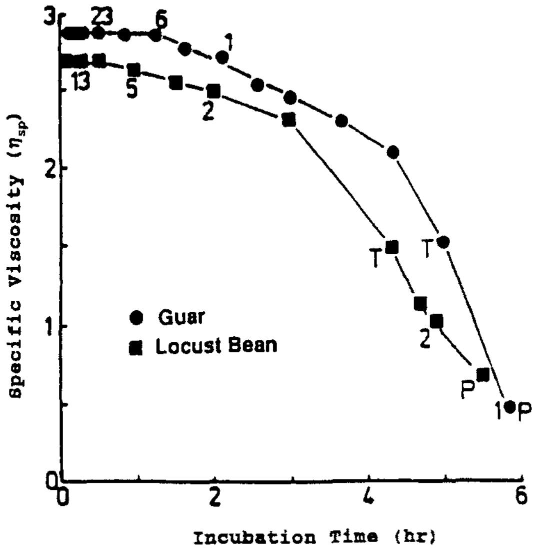

FIG. 14. EFFECT OF GALACTOSE REMOVAL ON SPECIFIC VISCOSITY OF GALACTOMANNAN SOLUTIONS
T = Turbid; P = Precipitated. Numbers represent the galactose content (%) of galactomannans. *From McCleary and Neukom 1982*

tion of the mannan backbone as presented in Fig. 15B, a single curve is obtained independent of the galactose content, indicating that the solution viscosity of such galactomannans is totally dependent on the nature of the mannan backbone in dilute solution. therefore, it is thought that the single galactose sidechains are not a significant rheological contributor in dilute solutions. McCleary and Neukom (1982) stated that the galactose sidechains played an important role in determining solubility of galactomannans, but they did not affect the degree of interaction between galactomannan molecules in dilute solution, nor did they have any apparent effect on the conformation of galactomannan molecules in solution. However, the contribution of galactose side chains in concentrated region ($c > c^*$), in which the polymer molecules are significantly entangled, was not studied.

On the other hand, Robinson *et al.* (1982) investigated $\eta_{sp}$ vs. $c[\eta]$ relationship for guar and locust bean galactomannans in both dilute and concentrated regions. Here the dimensionless "coil overlap parameter", $c[\eta]$, is a measure of the extent of overlapping between polymer molecules (Morris and Ross-Murphy 1981). It was reported that the slopes in the dilute domain ($c[\eta] < c^*[\eta]$) were approximately 1.3 similar to other polysaccharides (Launay *et al.* 1986). In contrast, the slopes were 5.1 in the concentrated region ($c[\eta] > c^*[\eta]$), which

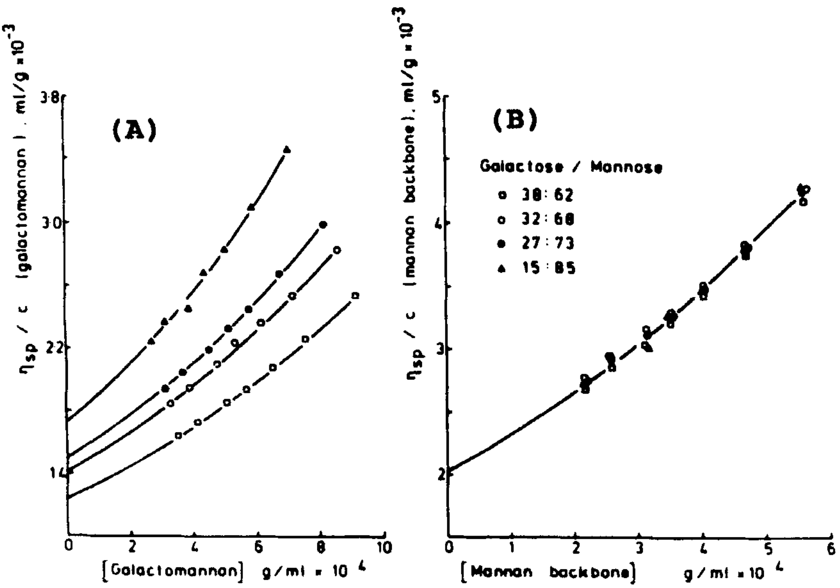

FIG. 15. EFFECT OF GALACTOSE REMOVAL FROM GUAR GALATOMANNAN ON INTRINSIC VISCOSITY AS A FUNCTION OF (A) GALACTOMANNAN CONCENTRATION AND (B) MANNAN MAIN BACKBONE CONCENTRATION
*From McCleary and Neukom 1982*

is significantly higher than the values of 3.3 ± 0.3 reported for other random coil polysaccharides by Morris *et al.* (1981). These results can be ascribed to the occurrence, in addition to normal topological entanglements, of specific interactions, called hyperentanglements, from sparing-substituted regions of mannan backbone packing together into ordered assemblies to the junction zones (Morris 1989). These results suggest that the distribution of galactose side branches affects entanglements of the galactomannan molecules in the concentrated region.

## Xanthan

Xanthan is an extracellular polysaccharide produced by the bacteria *Xanthomonas campestris* on the glucose medium (McNeely and Kang 1973). The molecular structure of xanthan is shown in Fig. 16 as determined by Jansson *et al.* (1975) and Melton *et al.* (1976). The main backbone of xanthan is composed of β-(1,4)-linked D-glucose units, which is thus essentially identical to the structure of cellulose. In contrast to cellulose which has no substituent groups, the trisaccharide sidechains consisting of one glucuronic acid and two mannose residues are attached to the cellulose backbone at 0–3 of alternative β-D-glu-

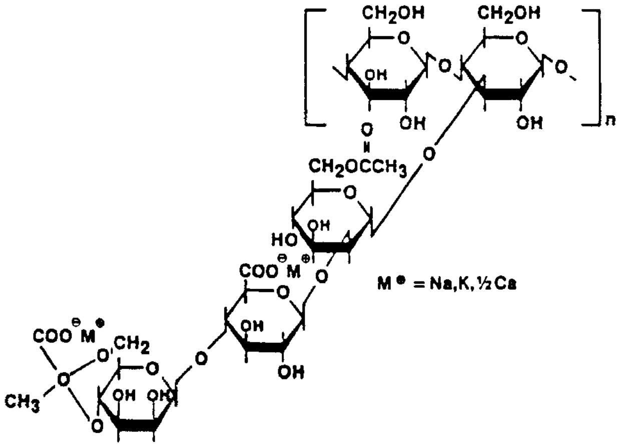

FIG. 16. STRUCTURE OF XANTHAN
*From Sanderson 1982*

copyranose residues (Pettitt 1979). The exact structure of the sidechains is as follows: [terminal D-mannose] – β(1,4) – [D-glucuronic acid] – β(1,2) – [internal D-mannose] – α(1,3) – [cellulose backbone] (Sanderson 1982). These sidechains compactly fold down against the cellulose backbone, leading to formation of a 5-fold ordered structure rather than the 2-fold conformation adopted by unsubstituted cellulose (Robinson *et al.* 1988). Some of the internal mannose groups are substituted at C-6 with acetyl groups, and approximately half of the terminal mannose residues may carry a pyruvate group linked at 0-4,6 as a ketal (Kovacs and Kang 1977). Cellulose, or equivalently the main backbone of xanthan, is completely water-insoluble due to a parallel array of molecules in crystalline arrangement through hydrogen bonding (Whistler and Daniel 1985). However, the addition of charged trisaccharide sidechains to the cellulose backbone solubilizes the xanthan molecules in either cold or hot water (Pettitt 1979).

Callet *et al.* (1987) demonstrated that in dilute solutions ($c < c^*$) the acetyl and pyruvate groups of xanthan had no influence on the solution viscosity when compared to native xanthan, as shown in Fig. 17. This is consistent with the report of Bradshaw *et al.* (1983) and Milas *et al.* (1986). Smith *et al.* (1984) stated that at concentrated solutions (typically ~1% w/v) the viscosity 'high-pyruvate' xanthan was significantly enhanced by the addition of salt, whereas that of 'low-pyruvate' xanthan was not. This argument was supported by the work of Cheetham and Nik Norma (1989). Tako and Nakamura (1984) investigated the dynamic viscoelastic properties of native and deacetylated xanthan as a function of concentration. The results are demonstrated in Fig. 18. The dynamic viscosity ($\eta'$) and storage modulus ($G'$) of deacetylated xanthan are

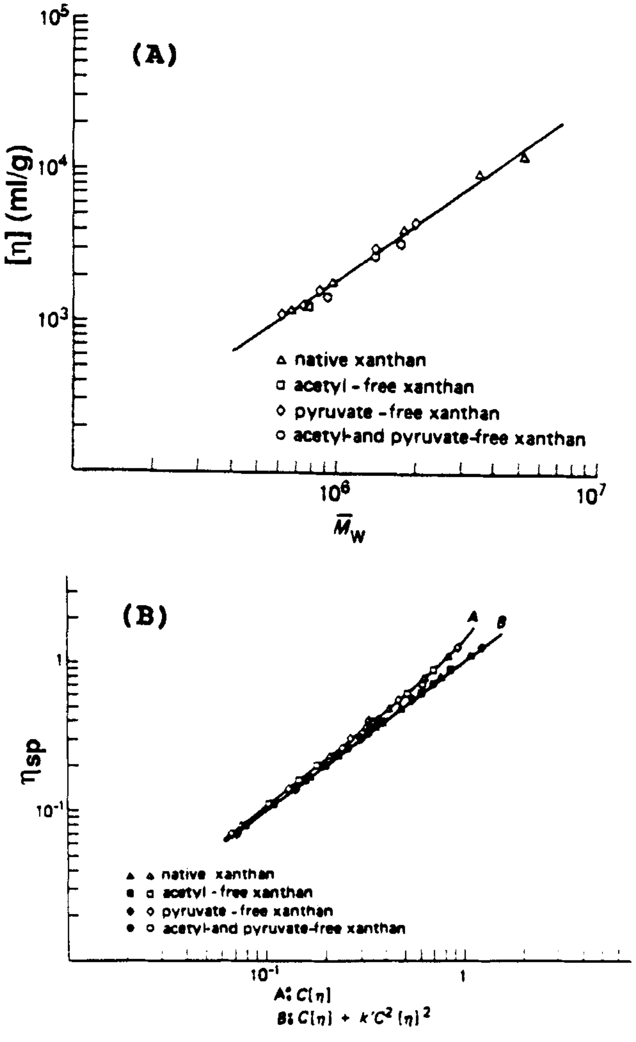

FIG. 17. (A) [η] VS. $M_w$ AND (B) $\eta_{sp}$ VS. c[η] (UNFILLED SYMBOLS) OR c[η] + $k'c^2[\eta]^2$ (FILLED SYMBOLS) OF THE 4 DIFFERENT XANTHAN SAMPLES IN 0.1 M NACL SOLUTION AT 25°C
*From Callet et al. 1987*

lower than those of native xanthan below approximately 0.3% and 0.5% of concentrations, respectively, above which the trend is however reversed. Such a phenomenon can be attributed to the formation of more intense intermolecular association of deacetylated xanthan molecules in concentrated solutions due to

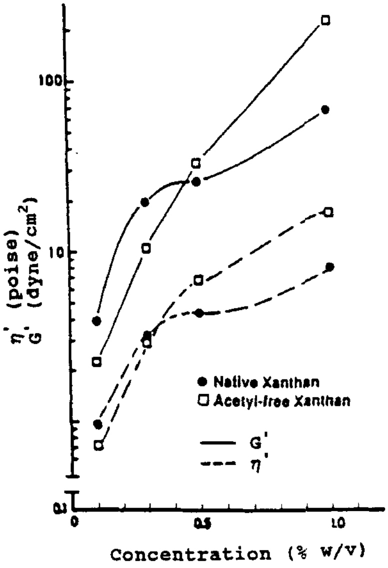

FIG. 18. DYNAMIC VISCOELASTICITY OF NATIVE AND DEACETYLATED XANTHAN SOLUTIONS AS A FUNCTION OF CONCENTRATION
*From Tako and Nakamura 1984*

greater sidechain mobility and/or backbone flexibility than the native xanthan (Tako and Nakamura 1986; Cheetham and Nashimba 1988). Therefore, the effects of acetyl and pyruvate groups on the solution viscosity might be influenced by the polymer concentration and the presence of salt. Tako and Nakamura (1984) also showed that the dynamic viscoelasticity of native xanthan solutions was nearly independent in the range of pH 5–11, whereas deacetylated xanthan exhibited the enhanced viscoelasticity in the acidic region, and vice versa in the alkaline region. These results suggest the occurrence of conformational changes after deacetylation. Callet *et al.* (1987) and Shatwell *et al.* (1990) demonstrated that acetyl groups exhibited a stabilizing effect on the ordered conformation of xanthan, whereas pyruvate groups destabilized the structure and lowered the melting temperature. The stabilizing influence of the pyruvate substituents is the result of charge-charge repulsion between the trisaccharide sidechains, but the reason for the stabilizing effect of the acetyl groups is unclear (Shatwell *et al.* 1990). Millane and Narasaiah (1990) reported that removal of the sidechain terminal mannose unit did not critically affect the stability of the xanthan ordered structure. However, the contribution of the trisaccharide sidechains to the rheological properties has not been investigated.

Both galactomannans and xanthan are nongelling polysaccharides in water. However, mixtures of locust bean gum and xanthan interact strongly, leading to the formation of a three-dimensional elastic gel (Dea *et al.* 1977; Morris *et al.* 1977; McCleary *et al.* 1981, 1985; Morris 1986). In contrast to locust bean gum, guar gum having the more branched structure shows only a very limited interaction with xanthan, resulting in viscosity enhancement rather than gelation (Tako and Nakamura 1985; Shatwell *et al.* 1991a). McCleary *et al.* (1981) and McCleary and Neukom (1982) investigated the interaction properties of galactomannans containing different degrees of G/M ratios with xanthan. It was reported that the viscosities were increased with decreasing G/M ratios, since galactomannan less-substituted with galactose conferred more regions for gelling interaction between galactomannan and xanthan. These results indicate that the extent of side branches of galactomannans influences significantly the gelling and corresponding rheological properties in these mixtures. The interaction is strongly affected by the galactose distribution pattern as well as the galactose content of galactomannan (McCleary *et al.* 1981, 1984b; Clark *et al.* 1986; Dea *et al.* 1986). McCleary (1979) showed that galactomannans interacted with the xanthan double helix in the region of the galactomannan backbone depleted in galactose residues and/or substituted on only one side with galactose. Tako *et al.* (1984) and Tako and Nakamura (1986) proposed a key-and-lock interacting mechanism, in which the xanthan trisaccharide sidechains in the helical conformation are inserted into the adjacent unsubstituted regions of the galactomannan backbone. Thus, the intermolecular interactions occur between the sidechains of xanthan and the unsubstituted mannan backbone of galactomannan. Tako *et al.* (1984) also demonstrated that deacetylated and thus more flexible xanthan molecules exhibited the stronger intermolecular interactions with locust bean galactomannan than the native xanthan. Very recently, Shatwell *et al.* (1991b) reported that removal of the terminal mannose residue from xanthan resulted in forming an exceptionally weak gel network with locust bean galatomannan as compared to the native xanthan. These results suggest that the xanthan trisaccharide sidechains might play an important role in interacting with locust bean galactomannan. Alternatively, based on the X-ray diffraction fiber studies, Cairns *et al.* (1986, 1987) and Brownsey *et al.* (1988) proposed a sandwich-type model, in which several galactomannan molecules may be inserted between the xanthan backbone. They observed that a mixture of xanthan and galactomannan did not form gelation until they were heated above the helix-coil transition temperature ($T_c$) of xanthan and then cooled. Thus, the interactions occur mostly between the cellulose backbone of xanthan in the disordered or nonhelical form and the unsubstituted mannan backbone of the galactomannan. This model is consistent with the report of Cheetham and Mashimba (1988). Cairns *et al.* (1987) also claimed that the xanthan trisaccharide sidechains would tend to inhibit the intermolecular association, which is contradictory to the observations of Tako *et* *al.* (1984) and Tako and Nakamura (1986). To summarize, the inhibitory effect of the galactose sidechains of galactomannan on the interactions with xanthan is well established, but the role of the xanthan trisaccharide sidechains and in particular the acetyl and pyruvic acid substituents that they carry is as yet poorly understood (Shatwell *et al.* 1991b).

## Pectin

Pectins, found in the primary cell wall and the intercellular middle lamellae region of plant tissues, are key substances responsible for the mechanical strength of the primary cell wall of fruits and vegetables and for adhesion between cells (Ilker and Szczesniak 1990). They are essentially composed of a linear α-(1,4)-linked D-galacturonic acid backbone, in which varying proportions of the galacturonic carboxyl groups are present as the methyl esters, and α-(1,2)-linked L-rhamnosyl residues are inserted at intervals to form rhamnogalacturonan (John and Dey 1986). Pectin molecules can be divided into two distinct regions; the homogalacturonan "smooth region" and the ehamnogalacturonan "hairy region" due to the covalently attached neutral side branches (De Vries *et al.* 1982, 1983).

The structural characteristics of pectins are summarized in Table 3. Side branches, consisting mainly of D-galactose, L-arabinose, D-xylose, and less frequently D-mannose, L-fucose, D-glucuronic acid, and the rather rare sugars 2-O-methyl-D-xylose, 2-O-methyl-L-fucose and D-apiose, are covalently attached to the main backbone primarily through C-4 of the rhamnosyl residues, although substitution of the galacturonyl residues at either C-2 or C-3 is also

TABLE 3.
STRUCTURAL CHARACTERISTICS OF PECTIN MOLECULES

| | |
|---|---|
| **Main Backbone** | Galacturonan<br>Rhamnogalacturonan |
| **Major Side Chains** | Arabinan<br>Galactan<br>Arabinogalactan |
| **Minor Side Chains** | β-D-Xyl-(1,3)-<br>L-Ara-(1,3)-<br>β-D-Gal-(1,2)-β-D-Xyl-(1,3)-<br>α-L-Fuc-(1,2)-β-D-Xyl-(1,3)-<br>D-Api-(1,3)-D-Api-(1-<br>β-D-GlcA-(1,4)-L-Fuc-(1-<br>β-D-GlcA-(1,6)-D-Gal-(1- |

found (Talmadge *et al.* 1973; Selvendran *et al.* 1987; Olsen *et al.* 1987; Bacic *et al.* 1988). The methylated sugars occur exclusively as end groups (Aspinall 1980). Most of these sugars occur in short branches, but the more common neutral constituents, D-galactose and L-arabinose, are also found in multiple units as galactan, arabinan and arabinogalactan (Aspinall 1980). Arabinan consisting of α-(1,5)-linked L-arabinose units displays a highly branched structure. In contrast, galactan is composed of β-(1,4)-linked galactose residues in a relatively linear form. Therefore, side branches of pectins can be characterized in terms of heterogeneity and significant dimension.

When compared to other branched carbohydrates, the contribution of side branches to the functional properties of pectins has been rarely studied. Recently, Matthew *et al.* (1990) reported that reduction in side branches, especially the arabinose content, enhanced considerably gelling properties of sugar beet pectins. Reid (1983) and BeMiller (1986) described that side branches of pectins may tend to limit the extent of interchain association. It is therefore thought that the intermolecular association promoted by the removal of side branches results in enhancing the formation of junction zones for gelling of sugar beet pectins. A good knowledge of the chemical structure and solution behavior of pectins (structure-property relationship) is of primary importance from a technological point of view and also to understand the role of pectic substances in the cell walls (Hourdet and Muller 1987). However, information on the branching contribution to solution properties of pectins is extremely scarce.

The rheological theories developed in synthetic polymers can be more successfully applicable to pectin solutions, since pectin molecules contain the significant dimension of side branches relative to other branched carbohydrates. Hwang and Kokini (1990a) investigated the contribution of side branches to the rheological properties of pectins with respect to $\eta_{sp}$ vs $c[\eta]$ relationship, zero shear viscosity, shear rate dependence of viscosity and elastic properties in terms of $G'$. It was found that the slopes of $\eta_{sp}$ vs $c[\eta]$ curve were nearly similar in the dilute solution region ($c[\eta] < c^*[\eta]$) regardless of the extent of side branches. In contrast, the higher branched pectins imparted the higher slopes in the concentrated region ($c[\eta] > c^*[\eta]$), indicating the contribution of side branches to entanglements. Increase in branching of pectins resulted in higher $\eta_O$, increasing shear rate dependence of viscosity and higher $G'$. Based on the rheological concept devised in synthetic polymers, it is postulated that side branches of pectins might be significantly involved in entanglements of the pectin molecules in the concentrated region (Hwang and Kokini 1990b).

## CONCLUSION

Rheological properties influenced by branching are summarized in Table 4 in conjunction with other physicochemical properties. Besides rheological prop-

TABLE 4.
COMPARISON OF RHEOLOGICAL AND OTHER PHYSICOCHEMICAL PROPERTIES OF LINEAR AND BRANCHED POLYMERS*

| Properties | Linear | Branched | References |
|---|---|---|---|
| Radius of Gyration | High | Low | Graessley (1968) |
| Intrinsic Viscosity | High | Low | Graessley (1968) |
| Zero-Shear Viscosity** | Low | High | Graessley (1977) |
| Zero-Shear Recoverable Compliance** | Low | High | Graessley (1982a) |
| Shear Rate Dependence of Viscosity | Low | High | Graessley (1984) |
| Extensional Viscosity | Low | High | Cogswell (1981) |
| Thermal Sensitivity of Viscosity | Low | High | Jacovic *et al.* (1979) |
| Solubility | Low | High | Billmeyer (1984) |
| Crystallinity | High | Low | Rodriguez (1970) |
| $T_m$, $T_g$ | High | Low | Nielsen (1969) |

* At the same molecular weight

** Based on significant entanglements of the branches

erties, the solubility, crystallinity and thermal properties represented by $T_g$ and $T_m$ can be also affected by branching. The presence of side branches enhances the solubility, since they prevent intermolecular association (Billmeyer 1984). Branched polymers are less crystallizable than linear polymers, since the branches prevent intermolecular alignment for crystallization. For example, crystallinity of linear HDPE is more than 90%, whereas that of branched LDPE is approximately 40–60% (Rodriguez 1970; Billmeyer 1984). In addition, branched polymers exhibit lower glass transition ($T_g$) and melting ($T_m$) temperatures as compared to linear polymers, since the branches function to increase free volume between polymer molecules (Nielsen 1969). $T_m$ of branched LDPE was reported to be 100–110°C, which was lower than 125–135°C of linear HDPE (Seymour and Carraher 1984; Mascia 1989).

This review clearly demonstrates that branching is a crucial contributor to the rheological properties in both synthetic and carbohydrate polymers. The rheological properties are influenced by the combined effects of the molecular weight, concentration and branching structure in terms of the number, distribution and length. Despite some advances made in star-branched polymers, complete molecular and rheological theories concerning the branching effects have not as yet been systematically established to comprise all types of branched synthetic polymers (Roovers 1985a; Marrucci 1989; Douglas *et al.* 1990). To our best knowledge, the significance of branching in biopolymers including carbohydrates has been disregarded with respects of its rheological contribution. Therefore, even though the rheological and other physicochemical theories devised in synthetic polymers are somewhat qualitative and phenomenological, it is anticipated that they can be effectively utilized to understand the physical phenomena of food systems containing branched biopolymers.

Understanding of the rheological theories governing branched polymers might provide guidelines for modification of rheological properties of polysaccharides. To date modification of polysaccharides has been confined to incorporation of short side branches and ionic functional groups, since most functional properties are sufficiently affected by the presence of short branches. As discussed in the text, the rheological properties might be more significantly influenced by long side branches. Thus, modification of the rheological properties of polysaccharides necessitates development of chemical and enzymatic means to attach long side branches to the main backbone. Alternatively, in the long term, genetic means might be employed for *in situ* modification of side branches in the plant cell wall. Polysaccharides with the modified branching structure can be characterized by applying the rheological concepts demonstrated in this review.

## ACKNOWLEDGMENT

This is paper D-10411-5-90 of the New Jersey Experimental Station. This work was supported by the Campbell Soup Co., and their support is greatly appreciated.

## REFERENCES

ASPINALL, G. O. 1980. Chemistry of cell wall polysaccharides. In *The Biochemistry of Plants, Vol. 3* (J. Preiss, ed.) pp. 480–486, Academic Press, New York.

AU-YEUNG, V. S., MACOSKO, C. W. and RAJU, V. R. 1981. Extensional flow of linear and star-branched hydrogenated polybutadiene with narrow molecular weight distribution. J. Rheol. *25,* 445–452.

BACIC, A., HARRIS, P. J. and STONE, B. A. 1988. Structure and function of plant cell walls. In *The Biochemistry of Plants, Vol. 14* (J. Preiss, ed.) pp. 309–314, Academic Press, New York.

BAKER, C. W. and WHISTLER, R. L. 1975. Distribution of D-galactosyl groups in guaran and locust-bean gum. Carbohydr. Res. *45,* 237–243.

BANKS, W. and MUIR, D. D. 1980. Structure and chemistry of the starch granule. In *The Biochemistry of Plants, Vol. 3* (J. Preiss, ed.) pp. 321–369, Academic Press, New York.

BARNES, H. A., HUTTON, J. F. and WALTERS, K. 1989. *An Introduction to Rheology,* pp. 75–77, 89–95, Elsevier Applied Science Publishers, New York.

BEMILLER, J. N. 1986. An introduction to pectins: structure and properties. In *Chemistry and Function of Pectins* (M. L. Fishman and J. J. Jen, eds.) p. 4, American Chemical Society, Washington, DC.

BERRY, G. C. 1971. Thermodynamics and conformational properties of polystyrene. III. Dilute solution studies on branched polymers. J. Polym. Sci. Part A-2 *9*, 687–715.

BERRY, G. C. and FOX, T. G. 1968. The viscosity of polymers and their concentrated solutions. Adv. Polym. Sci. *5*, 261–357.

BILLMEYER, F. W. 1984. *Textbook of Polymer Science,* 3rd ed., pp. 157, 179, 361–367, John Wiley & Sons, New York.

BIRD, R. B., ARMSTRONG, R. C. and HASSAGER, O. 1977. *Dynamics of Polymeric Liquids. Vol. 1. Fluid Dynamics,* pp. 77, 163, John Wiley & Sons, New York.

BRADSHAW, I. J., NISBET, B. A., KERR, M. H. and SUTHERLAND, I. W. 1983. Modified xanthan—its preparation and viscosity. Carbohydr. Polym. *3*, 23–38.

BROWNSEY, G. J., CAIRNS, P., MILES, M. J. and MORRIS, V. J. 1988. Studies on the mechanism of gelation for xanthan-galactomannan and xanthan-glucomannan mixed gels. In *Gums and Stabilizers for the Food Industry 4* (G. O. Phillips, P. A. Williams and D. J. Wedlock, eds.) pp. 157–163, IRL Press, Oxford.

BUECHE, F. 1964. Viscosity of molten branched polymers and their concentrated solutions. J. Chem. Phys. *40*, 484–487.

BURCHARD, W. 1983. Static and dynamic light scattering from branched polymers and biopolymers. Adv. Polym. Sci. *48*, 1–124.

BYWATER, S. 1979. Preparation and properties of star-branched polymers. Adv. Polym. Sci. *30*, 89–116.

CAIRNS, P., MILES, M. J. and MORRIS, V. J. 1986. Intermolecular binding of xanthan gum and carob gum. Nature *322*, 89–90.

CAIRNS, P., MILES, M. J., MORRIS, V. J. and BROWNSEY, G. J. 1987. X-ray fiber-diffraction studies of synergistic, binary polysaccharide gels. Carbohydr. Res. *160*, 411–423.

CALLET, F., MILAS, M. and RINAUDO, M. 1987. Influence of acetyl and pyruvate contents on rheological properties of xanthan in dilute solution. Int. J. Biol. Macromol. *9*, 291–293.

CHEETHAM, N.W.H. and MASHIMBA, E.N.M. 1988. Conformational aspects of xanthan-galactomannan gelation. Carbohydr. Polym. *9*, 195–212.

CHEETHAM, N.W.H. and NIK NORMA, N. M. 1989. The effect of pyruvate on viscosity properties of xanthan. Carbohydr. Polym. *10*, 55–60.

CHILD, T. F. and PRYCE, N. G. 1972. Steady-state and pulsed NMR studies of gelation in aqueous agarose. Biopolymers *11*, 409–429.

CLARK, A. M., DEA, I.C.M. and McCLEARY, B. V. 1986. The effect of galactomannan fine structure on their interaction properties. In *Gums and Stabilizers for the Food Industry 3* (G. O. Phillips, D. J. Wedlock. and P. A. Williams, eds.) pp. 429–431, Elsevier Applied Science Publishers, London.

COGSWELL, F. N. 1972. Converging flow of polymer melts in extrusion dies. Polym. Eng. Sci. *12,* 64–73.

COGSWELL, F. N. 1981. *Polymer Melt Rheology: A Guide for Industrial Practice,* pp. 81–83, John Wiley & Sons, New York.

DARBY, R. D. 1976. *Viscoelastic Fluids: An Introduction to Their Properties and Behavior,* p. 29, Marcel Dekker, New York.

DEA, I.C.M. 1987. The role of structural modification in controlling polysaccharide functionality. In *Industrial Polysaccharides: Genetic Engineering, Structure/Property Relations and Applications* (M. Yalpani, ed.) pp. 207–216, Elsevier Applied Science Publishers, New York.

DEA, I.C.M., CLARK, A. H. and McCLEARY, B. V. 1986. Effect of galactose-substitution-patterns on the interaction properties of galactomannans. Carbohydr. Res. *147,* 275–294.

DEA, I.C.M., McKINNON, A. A. and REES, D. A. 1972. Tertiary and quaternary structure in aqueous polysaccharide systems which model cell wall cohesion: reversible changes in conformation and association of agarose, carrageenan and galactomannan. J. Mol. Biol. *68,* 153–172.

DEA, I.C.M., MORRIS, E. R., REES, D. A., WELSH, E. J., BARNES, H. A. and PRICE, J. 1977. Associations of like and unlike polysaccharides: mechanism and specificity in galactomannans, interacting bacterial polysaccharides, and related systems. Carbohydr. Res. *57,* 249–272.

DE GENNES, P. G. 1971. Reptation of a polymer chain in the presence of fixed obstacles. J. Chem. Phys. *55,* 572–579.

DE VRIES, J. A., DEN VIJL, C. H., VORAGEN, A.G.J., ROMBOUTS, F. M. and PILNIK, W. 1983. Structural features of the neutral sugar side chains of apple pectic substances. Carbohydr. Polym. *3,* 193–205.

DE VRIES, J. A., ROMBOUTS, F. M., VORAGEN, A.G.J. and PILNIK, W. 1982. Enzymic degradation of apple pectins. Carbohydr. Polym. *2,* 25–33.

DOI, M. 1981. Explanation for the 3.4 power law of viscosity of polymeric liquids on the basis of the tube model. J. Polym. Sci. Polym. Lett. Ed. *19,* 265–273.

DOI, M. and EDWARDS, S. F. 1978. Dynamics of concentrated systems. Parts 1-4. J. Chem. Soc. Faraday Trans. II. *74,* 1789–1801, 1802–1817, 1818–1832; *75,* 38–54.

DOI, M. and KUZUU, N. Y. 1980. Rheology of star polymers in concentrated solutions and melts. J. Polym. Sci. Polym. Lett. Ed. *18,* 775–780.

DOUGLAS, J. F., ROOVERS, J. and FREED, K. F. 1990. Characterization of branching architecture through "universal" ratios of polymer solution properties. Macromolecules *23*, 4168–4180.

DUTTON, G.G.S. 1985. Polysaccharides. In *Encyclopedia of Polymer Science and Engineering, Vol. 13* (A. Klingsberg and T. Baldwin, eds.) pp. 87–147, John Wiley & Sons, New York.

FERRY, J. D. 1980. *Viscoelastic Properties of Polymers,* pp. 76, 232–233, John Wiley & Sons, New York.

FLEISCHER, G. 1985. Self-diffusion of long-chain branched polyethylenes in the melt. Polym. Comm. *26*, 359–361.

FLORY, P. J. 1953. *Principles of Polymer Chemistry,* pp. 402–410, 611, Cornell University Press, Ithaca.

FRENCH, D. 1984. Physical and chemical organization of starch granules. In *Starch: Chemistry and Technology,* 2nd ed. (R. L. Whistler, E. F. Paschall and J. N. BeMiller, eds.) Academic Press, New York.

FUJIMOTO, T., NARUKAWA, H. and NAGASAWA, M. 1970. Viscoelastic properties of comb-shaped polystyrene. Macromolecules *3*, 57–64.

GALLIARD, T. and BOWLER, P. 1987. Morphology and composition of starch. In *Starch: Properties and Potential* (T. Galliard, ed.) pp. 65–66, John Wiley & Sons, New York.

GLICKSMAN, M. 1986. *Hydrocolloids, Vol. III* (M. Glicksman, ed.) pp. 4–7, 157–158, CRC Press, Boca Raton, FL.

GRAESSLEY, W. W. 1968. Detection and measurement of branching in polymers. In *Characterization of Macromolecular Structure,* pp. 371–379, National Academy of Sciences, Washington, DC.

GRAESSLEY, W. W. 1974. The entanglement concept in polymer rheology. Adv. Polym. Sci. *16*, 1–179.

GRAESSLEY, W. W. 1977. Effect of long branches on the flow properties of polymers. Accoun. Chem. Res. *10*, 332–339.

GRAESSLEY, W. W. 1982a. Entangled linear, branched and network polymer systems-molecular theories. Adv. Polym. Sci. *47*, 67–117.

GRAESSLEY, W. W. 1982b. Effect of long branches on the temperature dependence of viscoelastic properties in polymer melts. Macromolecules *15*, 1164–1167.

GRAESSLEY, W. W. 1984. Viscoelasticity and flow in polymer melts and concentrated solutions. In *Physical Properties of Polymers* (J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern and J. L. Koenig, eds.) pp. 141–150, American Chemical Society, Washington, DC.

GRAESSLEY, W. W., MASUDA, T., ROOVERS, J.E.L. and HADJICHRISTIDIS, N. 1976. Rheological properties of linear and branched polystyrene. Macromolecules *9*, 127–141.

GRAESSLEY, W. W. and RAJU, V. R. 1984. Some rheological properties of solutions and blends of hydrogenated polybutadiene. J. Polym. Sci. Polym. Symp. *71*, 77–93.

GRAESSLEY, W. W. and ROOVERS, J. 1979. Melt rheology of four-arm and six-arm star polystyrenes. Macromolecules *12*, 959–965.

GRAESSLEY, W. W. and SHINBACH, E. S. 1974. Flow properties of branched polydisperse polymers. J. Polym. Sci. Polym. Phys. Ed. *12*, 2047–2063.

GRASDALEN, J. and PAINTER, T. J. 1980. N.M.R. studies of composition and sequence in legume-seed galactomannan. Carbohydr. Res. *81*, 59–66.

GREENWOOD, C. T. 1979. Observations on the structure of the starch granule. In *Polysaccharides in Food* (J.M.V. Blanshard and J. R. Mitchell, eds.) pp. 129–133, Butterworths, London.

GRUVER, J. T. and KRAUS, G. 1964. Rheological properties of polybutadienes prepared by n-butyllithium initiation. J. Polym. Sci. Part A *2*, 797–810.

GUPTA, A. K. and GRASDALEN, H. 1989. N.m.r. studies of composition and side-chain arrangement in *Sesbania aegyptiaca* seed galactomannan. Carbohydr. Res. *188*, 239–244.

HALL, L. D. and YALPANI, M. 1980. A high yielding, specific method for the chemical derivatization of D-galactose-containing polysaccharide: oxidation with D-galactose oxidase, followed by reductive amination. Carbohydr. Res. *81*, C10–C12.

HAM, J. S. 1957. Viscoelastic theory of branched and cross-linked polymer. J. Chem. Phys. *26*, 625–633.

HAN, C. D. 1976. *Rheology in Polymer Processing*, pp. 74–79, 206, 245, Academic Press, London.

HODGE, J. E. and OSMAN, E. M. 1976. Carbohydrates. In *Principles of Food Science: Part I.* (O. R. Fennema, ed.) pp. 100, 102–104, Marcel Dekker, New York.

HOOD, L. F. 1982. Current concepts of starch structure. In *Food Carbohydrates* (D. R. Lineback and G. E. Inglett, eds.) pp. 218–224, Van Nostrand Reinhold/AVI, New York.

HOURDET, D. and MULLER, G. 1987. Solution properties of pectin polysaccharides. I. Aqueous size exclusion chromatography of flax pectins. Carbohydr. Polym. *7*, 301–312.

HUI, P. A. and NEUKOM, H. 1964. Some properties of galactomannans. Tappi *47*, 39–42.

HWANG, J. and KOKINI, J. L. 1990a. Contribution of the side branches to rheological properties of pectins. Carbohydr. Polym. (submitted).

HWANG, J. and KOKINI, J. L. 1990b. Effect of the neutral sugar side chains on the rheological properties of pectins. Paper No. 704. presented at 50th Annual Meeting of IFT, Anaheim, CA, June 16–20.

ILKER, R. and SZCZESNIAK, A. S. 1990. Structural and chemical bases for texture of plant foodstuffs. J. Texture Stud. *21,* 1–36.

JACOVIC, M. S., POLLOCK, D. and PORTER, R. S. 1979. A rheological study of long branching in polyethylene by blending. J. Appl. Polym. Sci. *23,* 517–527.

JANSSON, P. E., KENNE, L. and LINDBERG, B. 1975. Structure of the extracellular polysaccharide from *Xanthomonas campestris*. Carbohydr. Res. *45,* 275–282.

JOHN, M. A. and DEY, P. M. 1986. Postharvest changes in fruit cell wall. Adv. Food Res. *30,* 139–193.

KENNEDY, J. F. and WHITE, C. A. 1983. *Bioactive carbohydrates: In Chemistry, Biochemistry and Biology,* pp. 42–45, 143, John Wiley & Sons, New York.

KIM, J. R. and REE, T. 1985. Dilute solution properties of branched polymers. J. Polym. Sci. Polym. Chem. Ed. *23,* 1119–1124.

KLEIN, J. 1986. Dynamics of entangled linear, branched, and cyclic polymers. Macromolecules *19,* 105–118.

KLEIN, J., FLETCHER, D. and FETTERS, L. J. 1983. Dynamics of entangled star-branched polymers. Faraday Symp. Chem. Soc. *18,* 159–191.

KOVACS, P. and KANG, K. S. 1977. Xanthan gum. In *Food Colloids* (H. D. Graham, ed.) pp. 504–505, Van Nostrand Reinhold/AVI, New York.

KRAUS, G. and GRUVER, J. T. 1965a. Rheological properties of cispolybutadiene. J. Appl. Polym. Sci. *9,* 739–755.

KRAUS, G. and GRUVER, J. T. 1965b. Rheological properties of multichain polybutadienes. J. Polym. Sci. Part A *3,* 105–122.

KRAUS, G. and GRUVER, J. T. 1970. Effect of diluents on the melt viscosity of branched polybutadienes. J. Polym. Sci. Part A-2 *8,* 305–310.

LARSON, R. G. 1988. *Constitutive Equations for Polymer Melts and Solutions,* pp. 104–106, Butterworths, Boston.

LAUN, H. M. and MÜNSTEDT, H. 1976. Comparison of the elongational behavior of a polyethylene melt at constant stress and constant strain rate. Rheol. Acta *15,* 517–524.

LAUN, H. M. and MÜNSTEDT, H. 1978. Elongational behavior of a low density melt. I. Strain rate and stress dependence of viscosity and recoverable strain in the steady-state. Comparison with shear rate. Influences of interfacial tension. Rheol. Acta *17,* 415–425.

LAUN, H. M. and SCHUCH, H. 1989. Transient elongational viscosities and drawability of polymer melts. J. Rheol. *33,* 119–175.

LAUNAY, B., DOUBLIER, J. L. and CUVELIER, G. 1986. Flow properties of aqueous solutions and dispersions of polysaccharides. In *Functional Properties of Food Macromolecules* (J. R. Mitchell and D. A. Ledward, eds.) p. 151, Elsevier Applied Science Publishers, London.

MA, C., WHITE, J. L., WEISSART, F. C. and MIN, K. 1985. Flow patterns in carbon black filled polyethylene at the entrance to die. J. Non-Newtonian Fluid Mech. *17*, 275–287.

MANNERS, D. J. 1989. Recent developments in our understanding of amylopectin structure. Carbohydr. Polym. *11*, 87–112.

MARCHESSAULT, R. H., BULEON, A., DESLANDES, Y. and GOTO, T. 1979. Composition of X-ray diffraction data of galactomannan. J. Colloid Interface Sci. *71*, 375–382.

MARRUCCI, G. 1989. Molecular modelling of flows of concentrated polymers. In *Transport Phenomena in Polymeric Systems* (R. A. Mashelker, A. S. Mujumdar and R. Kamal, eds.) p. 25, Ellis Horwood Ltd., New York.

MASUDA, T., OHTA, Y., KITAMURA, M., SAITO, Y., KATO, K. and ONOGI, S. 1981. Rheological properties of anionic polystyrenes. 7. Viscoelastic properties of six-branched star polystyrenes and their concentrated solutions. Macromolecules *14*, 354–360.

MASUDA, T., OHTA, Y. and ONOGI, S. 1971. Rheological properties of anionic polystyrene. III. Characterization and rheological properties of four-branch polystyrene. Macromolecules *4*, 763–768.

MASUDA, T., OHTA, Y., YAMAUCHI, T. and ONOGI, S. 1984. Characterization and rheological properties of multibranched star polyethylenes. Polym. J. *16*, 273–291.

MATTHEW, J. A., HOWSON, S. J., KEENAN, M. H. and BELTON, P. S. 1990. Improvement of the gelation properties of sugar beet pectin following treatment with an enzyme preparation derived from *Aspergillus niger*-comparison with a chemical modification. Carbohydr. Polym. *12*, 295–306.

McCLEARY, B. V. 1979. Enzymic hydrolysis, fine structure, and gelling interaction of legume-seed D-galacto-D-mannans. Carbohydr. Res. *71*, 205–230.

McCLEARY, B. V., AMADO, R., WAIBEL, R. and NEUKOM, H. 1981. Effect of galactose content on the solution and interaction properties of guar and carob galactomannans. Carbohydr. Res. *91*, 269–285.

McCLEARY, B. V., CLARK, A. H., DEA, I.C.M. and REES, D.A. 1985. The fine structure of carob and guar galactomannans. Carbohydr. Res. *139*, 237–260.

McCLEARY, B. V., DEA, I.C.M. and CLARK, A. H. 1984a. The fine structure of carob and guar galactomannans. In *Gums and Stabilizers for the Food Industry 2* (G. O. Phillips, D. J. Wedlock and P. A. Williams, eds.) pp. 33–34, Pergamon Press, Oxford.

McCLEARY, B. V., DEA, I.C.M., WINDUST, J. and COOKE, D. 1984b. Interaction properties of D-galactose-depleted guar galactomannan samples. Carbohydr. Polym. *4*, 253–270.

McCLEARY, B. V. and NEUKOM, H. 1982. Effect of enzymatic modification on the solution and interaction properties of galactomannans. Prog. Food Nutr. Sci. *6,* 109–118.

McLEISH, T.C.B. 1988. Molecular rheology of H-polymers. Macromolecules *21,* 1062–1070.

McNEELY, W. H. and KANG, K. S. 1973. Xanthan and some other biosynthetic gums. In *Industrial Gums, Polysaccharides and Their Derivatives,* 2nd ed. (R. L. Whistler and J. N. BeMiller, eds.) p. 486, Academic Press, New York.

MELTON, L. D., MINDT, L., REES, D. A. and DANDERSON, G. R. 1976. Covalent structure of the extracellular polysaccharide from *Xanthomonas campestris:* evidence from partial hydrolysis studies. Carbohydr. Res. *46,* 245–257.

MILAS, M., RINAUDO, M. and TINLAND, B. 1986. Role of the structure on the rheological behavior of xanthan gum. In *Gums and Stabilizers for the Food Industry 3* (G. O. Phillips, D. J. Wedlock and P. A. Williams, eds.) pp. 637–644, Elsevier Applied Science Publishers, London.

MILLANE, R. P. and NARASAIAH, T. V. 1990. X-ray fiber diffraction studies of a variant of xanthan gum in which the sidechain terminal mannose unit is absent. Carbohydr. Polym. *12,* 315–321.

MILTZ, J. and RAM, A. 1973. Flow behavior of well-characterized polyethylene melts. Polym. Eng. Sci. *13,* 273–279.

MINOSHIMA, W. and WHITE, J. L. 1986a. A comparative experimental study of the isothermal shear and uniaxial elongational rheological properties of low density, high density and linear low density polyethylenes. J. Non-Newtonian Fluid Mech. *19,* 251–274.

MINOSHIMA, W. and WHITE, J. L. 1986b. Instability phenomena in tubular film, melt spinning of rheologically characterized high density, low density and linear low density polyethylenes. J. Non-Newtonian Fluid Mech. *19,* 275–302.

MITCHELL, J. R. 1979. Rheology of polysaccharide solutions and gels. In *Polysaccharides in Food* (J.M.V. Blanshard and J. R. Mitchell, eds.) pp. 56, Butterworths, London.

MORRIS, E. R. 1989. Polysaccharide solution properties: origin, rheological characterization and implications for food systems. In *Frontiers in Carbohydrate Research-1: Food Applications* (R. P. Millane, J. N. BeMiller and R. Chandrasekaran, eds.) pp. 134–138, Elsevier Applied Science Publishers, London.

MORRIS, E. R., CUTLER, A. N., ROSS-MURPHY, S. B., REES, D. A. and PRICE, J. 1981. Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. Carbohydr. Polym. *1,* 5–21.

MORRIS, E. R., REES, D. A., YOUNG, G., WALKINSHAW, M. D. and DARKE, A. 1977. Order-disorder transition for a bacterial polysaccharide in solution. A role for polysaccharide conformation in recognition between *Xanthomonas* pathogen and its plant host. J. Mol. Biol. *110,* 1–16.

MORRIS, E. R. and ROSS-MURPHY, S. B. 1981. Chain flexibility of polysaccharides and glycoproteins from viscosity measurements. Tech. Carbohydr. Metab. *B310,* 1–46.

MORRIS, V. J. 1986. Gelation of polysaccharides. In *Functional Properties of Food Macromolecules* (J. R. Mitchell and D. A. Ledward, eds.) pp. 158–160, Elsevier Applied Science Publishers, London.

MORRIS, V. J. 1990. Starch gelation and retrogradation. Trends Food Sci. Technol. *1,* 2–6.

MÜNSTEDT, H. 1981. The influence of various deformation histories on elongational properties of low density polyethylene. Colloid & Polym. Sci. *259,* 966–972.

MÜNSTEDT, H. and LAUN, H. M. 1981. Elongational properties and molecular structure of polyethylene melts. Rheol. Acta *20,* 211–221.

NEUKOM, H. 1989. Galactomannans: properties and applications. Lebensm.-Wiss. u.-Technol. *22,* 41–45.

NIELSEN, L. E. 1969. Cross-linking effect on physical properties of polymers. J. Macromol. Sci. Rev. Macromol. Chem. *C3,* 69–103.

NIELSEN, L. E. 1977. *Polymer Rheology,* pp. 69–72, 80–82, Marcel Dekker, New York.

NORDMEIER, E., LANVER, U. and LECHNER, M. D. 1990. The molecular structure of low-density polyethylene. 1. Long-chain branching and solution properties. Macromolecules *23,* 1072–1076.

OLSEN, A., GRAY, G. M. and CHIU, M. C. 1987. Chemistry and analysis of soluble dietary fiber. Food Technol. *41,* 71–80.

OSAKI, K. 1973. Viscoelastic properties of dilute polymer solutions. Adv. Polym. Sci. *12,* 1–64.

OSAKI, K. and SCHRAG, J. 1973. Numerical calculations of the viscoelastic properties of solutions of branched polymers based on the Zimm-Kilb theory. J. Polym. Sci. Polym. Phys. Ed. *11,* 549–558.

PAINTER, T. J., GONZALEZ, J. J. and HEMMER, P. C. 1979. The distribution of D-galactosyl groups in guaran and locust-bean gum: new evidence from periodate oxidation. Carbohydr. Res. *69,* 217–226.

PALMER, K. J. and BALLANTYNE, M. T. 1950. The structure of (I) some pectin esters and (II) guar galactomannan. J. Am. Chem. Soc. *72,* 736–741.

PEARSON, D. S. and HELFAND, E. 1983. Rheological behaviors of branched polymer molecules. Faraday Symp. Chem. Soc. *18,* 189–197.

PEARSON, D. S. and HELFAND, E. 1984. Viscoelastic properties of star-branched polymers. Macromolecules *17,* 888–895.

PETTITT, D. J. 1979. Xanthan gum. In *Polysaccharides in Food* (J.M.V. Blanshard and J. R. Mitchell, eds.) pp. 265–267, Butterworth, London.

PORTER, R. S., KNOX, J. P. and JOHNSON, J. F. 1968. On the flow and activation energy of branched polyethylene melts. Trans. Soc. Rheol. *12,* 409–419.

RAJU, V. R., MENEZES, E. V., MARIN, G. and GRAESSLEY, W. W. 1981. Concentration and molecular weight dependence of viscoelastic properties in linear and star polymers. Macromolecules *14,* 1668–1676.

RAJU, V. R., SMITH, G. G., MARIN, G., KNOX, J. R. and GRAESSLEY, W. W. 1979. Properties of amorphous and crystallizable hydrocarbon polymers. I. Melt rheology of fractions of linear polyethylene. J. Polym. Sci. Polym. Phys. Ed. *17,* 1183–1195.

REID, D. S. 1983. Ionic polysaccharides. In *Developments in Ionic Polymers* (A. D. Wilson and J. Harvard, eds.) pp. 272–273, Elsevier Applied Science Publisher, London.

ROBIN, J. P., MERCIER, C., CHARBONNIERE, R. and GUILBOT, A. 1974. Lintenerized starches. Gel filteration and enzymatic studies of insoluble residue from prolonged acid treatment of potato starch. Cereal Chem. *51,* 389–406.

ROBINSON, G., MANNING, C. E., MORRIS, E. R. and DEA, I.C.M. 1988. Sidechain-mainchain interactions in bacterial polysaccharides. In *Gums and Stabilizers for the Food Industry 4* (G. O. Phillips, P. A. Williams and D. J. Wedlock, eds.) pp. 173–181, IRL Press, Oxford.

ROBINSON, G., ROSS-MURPHY, S. B. and MORRIS, E. R. 1982. Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan. Carbohydr. Res. *107,* 17–32.

RODRIGUEZ, F. 1970. *Principles of Polymer Systems,* p. 35, McGraw-Hill Book Co., New York.

ROKUDAI, M. 1979. Influence of shearing history on the rheological properties and processibility of branched polymers. J. Appl. Polym. Sci. *23,* 463–471.

ROOVERS, J. 1981. The steady-state shear compliance of regular star polymers. Polym. *22,* 1603–1605.

ROOVERS, J. 1984. Melt rheology of H-shaped polystyrenes. Macromolecules *17,* 1196–1200.

ROOVERS, J. 1985a. Branched polymers. In *Encyclopedia of Polymer Science and Engineering Vol. 2* (A. Klingsberg, J. Muldoon and A. Salvatore, eds.) pp. 478–499, John Wiley & Sons, New York.

ROOVERS, J. 1985b. Properties of the plateau zone of star-branched polybutadienes and polystyrenes. Polymers *26,* 1091–1095.

ROOVERS, J. and GRAESSLEY, W. W. 1981. Melt rheology of some model comb polystyrene. Macromolecules *14,* 766–773.

ROOVERS, J. and TOPOROWSKI, P. M. 1987. Relaxation by constraint release in combs and star-combs. Macromolecules *20,* 2300–2306.

ROUSE, P. E. 1953. A theory of the linear viscoelastic properties of dilute solutions of coiling polymer. J. Chem. Phys. *21,* 1272–1280.

SAMURKAS, T., LARSON, R. G. and DEALY, J. M. 1989. Strong extensional and shearing flow of a branched polyethylene. J. Rheol. *33,* 559–578.

SANDERSON, G. R. 1982. The interactions of xanthan gum in food systems. Prog. Food Nutr. Sci. *6,* 77–87.

SCHUERCH, C. 1985. Polysaccharides, synthetic. In *Encyclopedia of Polymer Science and Engineering, Vol. 13* (A. Klingsberg and T. Baldwin, eds.) pp. 147–162, John Wiley & Sons, New York.

SELVENDRAN, R. R., STEVENS, B.J.H. and DU PONT, M. S. 1987. Dietary fiber: chemistry, analysis, and properties. Adv. Food Res. *31,* 117–209.

SEYMOUR, R. B. and CARRAHER, C. E. 1984. *Structure-Property Relationships in Polymers,* p. 64, Plenum Press, New York.

SHATWELL, K. P., SUTHERLAND, I. W., DEA, I.C.M. and ROSS-MURPHY, S. B. 1990. The influence of acetyl and pyruvate substituents on the helix-coil transition behavior of xanthan. Carbohydr. Res. *206,* 87–103.

SHATWELL, K. P., SUTHERLAND, I. W., ROSS-MURPHY, S. B. and DEA, I.C.M. 1991a. Influence of the acetyl substituent on the interaction of xanthan with plant polysaccharide. II. Xanthan-guar gum systems. Carbohydr. Polym. *14,* 115–130.

SHATWELL, K. P., SUTHERLAND, I. W., ROSS-MURPHY, S. B. and DEA, I.C.M. 1991b. Influence of the acetyl substituent on the interaction of xanthan with plant polysaccharide. I. Xanthan-locust bean gum systems. Carbohydr. Polym. *14,* 29–51.

SMALL, P. A. 1975. Long-chain branching in polymers. Adv. Polym. Sci. *18,* 1–64.

SMIRNOVA, N. I. and SHCHERBUKHIN, V. D. 1989. Structure and $^{13}C$ NMR spectroscopy of galactomannan form *Indigofera tinctoria* seeds. Appl. Biochem. Microbiol. *25,* 185–190.

SMITH, P. S. 1982. Starch derivatives and their use in food. In *Food Carbohydrates* (D. R. Lineback and G. E. Inglett, eds.) pp. 247–248, Van Nostrand Reinhold/AVI, New York.

SMITH, I. H., SYMES, K. C., LAWSON, C. J. and MORRIS, E. R. 1984. The effect of pyruvate on xanthan solution properties. Carbohydr. Polym. *4,* 153–157.

SOSKEY, P. R. and WINTER, H. H. 1985. Equibiaxial extension of two polymer melts: polystyrene and low density polyethylene. J. Rheol. *29,* 493–517.

TAKAHASHI, Y., SUZUKI, F., MIYACHI, M., NODA, I. and NAGASAWA, M. 1986. Zero-shear viscosity of branched polymer solutions. Polym. J. *18,* 89–94.

TAKO, M., ASATO, A. and NAKAMURA, S. 1984. Rheological aspects of the intermolecular interaction between xanthan and locust bean gum in aqueous media. Agr. Biol. Chem. *48,* 2995–3000.

TAKO, M. and NAKAMURA, S. 1984. Rheological properties of deacetylated xanthan in aqueous media. Agr. Biol. Chem. *48,* 2987–2993.

TAKO, M. and NAKAMURA, S. 1985. Synergistic interaction between xanthan and guar gum. Carbohydr. Res. *138,* 207–213.

TAKO, M. and NAKAMURA, S. 1986. D-mannose-specific interaction between xanthan and D-galacto-D-mannan. FEBS Lett. *204,* 33–36.

TALMADGE, K. W., KEEGSTRA, K., BAUER, W. D. and ALBERSHEIM, P. 1973. The structure of plant cell walls. Plant Physiol. *51,* 158–173.

THURMOND, C. D. and ZIMM, B. H. 1952. Size and shape of the molecules in artificially branched polystyrene. J. Polym. Sci. *5,* 477–494.

THURN, A. anD BURCHARD, W. 1985. Heterogeneity in branching of amylopectin. Carbohydr. Polym. *5,* 441–460.

UTRACKI, L. A. and ROOVERS, J.E.L. 1973. Viscosity and normal stresses of linear and star branched polystyrene solutions. II. Shear-dependent properties. Macromolecules *6,* 373–377.

VALENTINE, R. H., FERRY, J. D., HOMMA, T. and NINOMIYA, K. 1968. Viscoelastic properties of polybutadienes-linear and lightly crosslinked near the gel point. J. Polym. Sci. Part A-2 *6,* 479–492.

VALLES, E. M. and MACOSKO, C. W. 1979. Structure and viscosity of poly(dimethylsiloxanes) with random branches. Macromolecules *12,* 521–526.

WHISTLER, R. L. and DANIEL, J. R. 1985. Carbohydrates. In *Food Chemistry* (O. R. Fennema, ed.) pp. 108–122, Marcel Dekker, New York.

WHITE, S. A. and BAIRD, D. G. 1986. The importance of extensional flow properties on planar entry flow patterns of polymer melts. J. Non-Newtonian Fluid Mech. *20,* 93–101.

WHITE, S. A., GOTSIS, A. D. and BAIRD, D. G. 1987. Review of the entry flow problem: experimental and numerical. J. Non-Newtonian Fluid Mech. *24,* 121–160.

WINTER, W. T., CHIEN, Y. Y. and BOUCKRIS, H. 1984. Structural aspects of food galactomannans. In *Gums and Stabilizers for the Food Industry 2* (G. O. Phillips, D. J. Wedlock and P. A. Williams, eds.) pp. 535–539, Pergamon Press, Oxford.

WURZBURG, O. B. 1986. Introduction. In *Modified Starches: Propeties and Uses* (O. B. Wurzburg, ed.) pp. 4–13, CRC Press, Boca Raton, Fl.

YALPANI, M. 1985. New approaches to the synthesis of branched polysaccharide derivatives for structure/function studies. In *New Developments in Industrial Polysaccharides* (V. Crescenzi, I.C.M. Dea and S. S. Stivala, eds.) pp. 295–306, Gordon and Breach Science Publishers, New York.

YALPANI, M. 1987. Progress in chemical modification of polysaccharides. In *Industrial Polysaccharides: Genetic Engineering, Structure/Property Relations and Applications* (M. Yalpani, ed.) pp. 121–127, Elsevier Applied Science Publishers, Amsterdam.

YALPANI, M. and DESROCHERS, M. J. 1987. Developments and prospects in enzymatic biopolymer modifications. In *Industrial Polysaccharides: Genetic Engineering, Structure/Property Relations and Applications* (M. Yalpani, ed.) pp. 7–34, Elsevier Applied Science Publishers, Amsterdam.

YU, L-P. and ROLLINGS, J. E. 1987. Low-angle laser light scattering-aqueous size exclusion chromatography of polysaccharides: Molecular weight distribution and polymer branching determination. J. Appl. Polym. Sci. *33*, 1909–1921.

YU, L-P. and ROLLINGS, J. E. 1988. Quantitative branching of linear and branched polysaccharide mixtures by size exclusion chromatograpy and on-line low-angle laser light scattering detection. J. Appl. Polym. Sci. *35*, 1085–1102.

ZIMM, B. H. 1956. Dynamics of polymer molecules in dilute solutions: viscoelasticity, flow refringence, and dielectric loss. J. Chem. Phys. *24*, 269–278.

ZIMM, B. H. and KILB, R. W. 1959. Dynamics of branched polymer molecules in dilute solution. J. Polym. Sci. *37*, 19–42.

ZIMM, B. H. and STOCKMAYER, W. H. 1949. The dimensions of chain molecules containing branches and rings. J. Chem. Phys. *17*, 1301–1314.

ZOBEL, H. F. 1988. Molecules to granules: a comprehensive starch review. Starch *40*, 44–50.