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can understand the correlation between MW and CC of the present high-conversion copolymer in Figures 2 and 4.

Moreover, the components of high MA content and of low MA content are produced at high and low conversion, respectively. The gel effect can affect the polymerization only at high conversion. Therefore, the amounts of the copolymer components are negligible in both regions of very high MW and low MA content and of very low MW and high MA content. On the other hand, the middle MW components can be produced at all conversions (and at all regions of MA content). These are the reasons for the broad CCD of the middle MW fractions.

In Figure 4, the MA content of the turning point of the ridge is found to be 48–49 mol %. From the copolymerization theory,[9] we can calculate the conversion corresponding to the MA content, by using the initial monomer composition, $f_{MA}{}^0 = 0.60$, and the monomer reactivity ratios, $r_{MA} = 0.18$ and $r_S = 0.75$.[10] The turning conversion is 23–31 wt %. We would like to point out that the gel effect became noticeable at the conversion of about 30 wt % in many cases.[11]

In general, the CCD determined by the TLC method may not be sufficiently accurate. However, we examined the reliability of the method for the present copolymer sample, comparing the CCD's obtained by the present method to those by the cross fractionation and by the theoretical calculation in the previous work.[6] The agreement among those results was satisfactory. As shown in Figure 3, the CCD curve composed by accumulating the CCD's of the fractions agreed approximately with that of the whole copolymer obtained in the previous work.[6] Moreover, the average MA contents of the respective fractions are in good agreement with the results by the analytical GPC, as shown in Figure 1.

Therefore, we would like to say that the results shown in Figure 2 are reliable enough for the qualitative discussion presented above.

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Liquid–Liquid Transition and Radiation-Induced Polymerization of Vinyl Acetate at High Pressure

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ABSTRACT: Pressure–volume–temperature (P–V–T) relations and the pressure dependence of the radiation-induced polymerization rate of vinyl acetate were measured. The specific volume of vinyl acetate changed discontinuously at pressures lower than the crystallization pressure: 170 MPa at 20 °C and 220 MPa at 30 °C. The discontinuous volume change became unclear with increasing temperature and disappeared at 40 °C. The P–V–T relation of methyl acetate, which does not contain a vinyl group, was measured for comparison with that of vinyl acetate. The specific volume of methyl acetate changed discontinuously with pressure in the same manner as that of vinyl acetate. It is considered from the P–V–T relations of the two compounds that these molecules align with planar –C–CO–O– groups and that molecular packings different from that in a normal (isotropic) liquid phase are realized above the pressure that gives discontinuous volume change (break pressure). As reported recently, the rate of polymerization of methyl acrylate, which is a structural isomer of vinyl acetate, changed discontinuously in accordance with the discontinuous volume change of the monomer, but the polymerization rate of vinyl acetate increased smoothly with pressure. A comparison of the present results with those of methyl acrylate led to a conception that the geometry and freedom of mobility between two planar groups affect the mode of pressure-induced alignment.

Introduction

High-pressure polymerization with radical initiator has been reported by many authors[1-5]. There has been difficulty in measuring the polymerization rate at the initial stage because polymerization reaction starts during compression and heating to reaction pressure and temperature. The radiation-induced method is prior to the initiator method in this point, because reaction can be started by γ-irradiation after the polymerization condition is established. We observed in radiation-induced high-pressure polymerization that vinyl monomers such as methacrylic esters,[6,7] acrylonitrile,[8] acrylic esters,[9] and styrene[10] show

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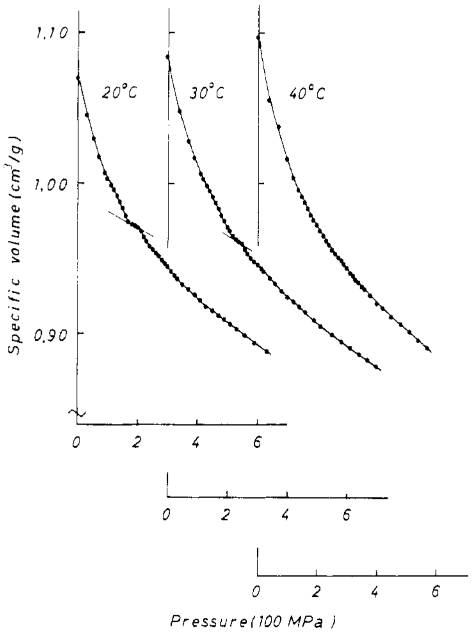

Figure 1. P–V relations of vinyl acetate at 20, 30, and 40 °C.

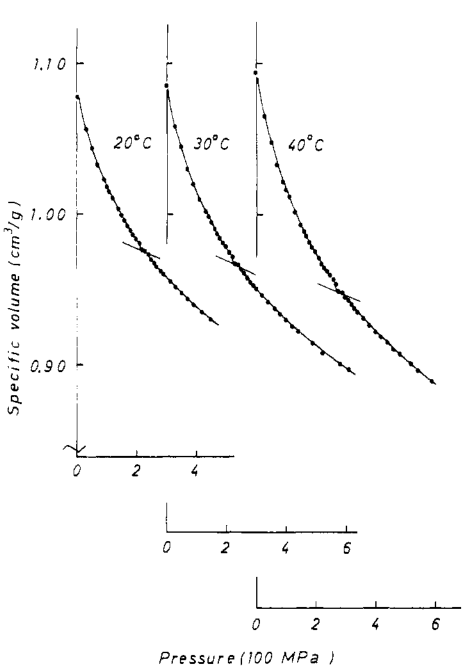

Figure 2. P–V relations of methyl acetate at 20, 30, and 40 °C.

a characteristic pressure dependence of polymerization rate. Activation volume in polymerization of these vinyl monomers shows discontinuous change at inherent pressure for each monomer. The specific volume of these monomers[8,9,11] and relaxation time T_1 of styrene[12] by pulse NMR measurement changed discontinuously at the pressure giving the change in activation volume. These results suggest a change in the physical state of the liquid monomer system at inherent pressure. Our conception is that the vinyl monomers align with their planar segments and the system turns to a mesophase at the characteristic pressure and temperature. We call the change in molecular packing induced by pressure "pressure-induced alignment". The pressure-induced alignment is believed to originate from alignment of planar vinyl and planar substituent groups. It is also believed that configurational freedom beteen vinyl and planar substituent groups plays an important role in the change in mode of pressure-induced alignment. In view of the effect of configurational freedom between vinyl and substituent groups on pressure-induced alignment, the P–V–T relation and pressure dependence of polymerization rate of vinyl acetate, which is a structural isomer of methyl acrylate, were studied. P–V–T relations of methyl acetate, which does not have a vinyl group, was also measured to confirm the role of the planar –C–CO–O– group on pressure-induced alignment.

Experimental Section

Materials used were reagent grade vinyl acetate and methyl acetate. These were purified by distillation under vacuum, and 0.01% hydroquinone was added as a polymerization inhibitor for P–V–T measurements. P–V–T measurement and polymerization were carried out with the glass dilatometer reported previously.[6] The sample was degassed by the freeze–thaw method several times ($\sim 10^{-3}$ torr) in the sample cell of the dilatometer on a vacuum line and then mercury was introduced under vacuum. The dilatometer was pressurized hydrostaticaly up to 700 MPa with the high-pressure apparatus reported elsewhere.[13] Change in volume caused by compression or polymerization was measured by detecting electrically the height of the mercury level in the capillary.[14] Pressure was increased and decreased stepwise at 10-MPa intervals. Dilatometric reading was carried out after the pressure and temperature were at a steady state. Calculation of a specific volume was carried out by the method reported previously.[14] Polymerization was initiated by irradiation of ^{60}Co γ-rays (7×10^3 rd/h for Fricke solution) after the pressure and temperature reached a steady state. The rate of polymerization was calculated from a volume–irradiation time curve and the final conversion by gravimetry.

Results and Discussion

***P*–*V*–*T* Relations.** Figure 1 shows the P–V isotherms of vinyl acetate at various temperatures. These isotherms are not smooth; the specific volume at 20 °C decreases monotonically up to 170 MPa and the compressibility abruptly decreases to about half those below 170 MPa in the pressure range 170–200 MPa. Above 200 MPa, the specific volume decreases again monotonically with relatively large compressibility. The profiles of the P–V isotherms at 30 and 40 °C are similar to the one at 20 °C, but the characteristic feature becomes unclear with increasing temperature. Similar characteristic P–V behavior has been observed in acrylonitrile,[8] acrylic esters,[9] and styrene.[11] The discontinuous volume change with pressure indicates a change in the physical state of the system. The pressure dependence of polymerization rate of the monomers mentioned above changed discontinuously, in accordance with characteristic behavior in P–V isotherms; activation volume changed discontinuously below and above the pressure giving a discontinuous volume change (break pressure). From this evidence, we propose that molecular packing in the liquid phase differs below and above the pressure giving the break in the P–V isotherm. The characteristic behavior in the P–V isotherm tends to be unclear with increasing temperature;[8,9,11] this is explained as the result of an increase in molecular motion at high temperature. The P–V relations and disappearance of the break of vinyl acetate at 40 °C are interpreted in a similar manner.

The P–V isotherms of methyl acetate shown in Figure 2 resemble those of vinyl acetate, and the discontinuous change in the P–V relations also indicates that the molecular packing differs below and above the break. This was the first case in the series in which the characteristic P–V behavior was observed in a compound that did not have a vinyl group. Methyl acetate consists of planar CH_3-CO-O- and $-CH_3$ groups as shown in Figure 3. This molecule is regarded to have a planar shape as a whole, because the molecular conformation is only varied by rotation of the methyl group around the C–O bond (A). It

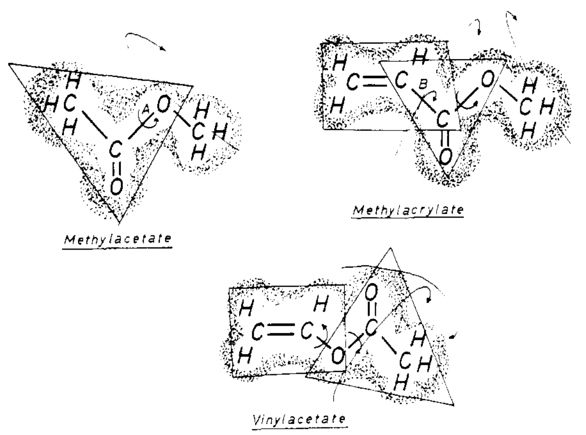

Figure 3. Schematic molecular models of methyl acetate, vinyl acetate, and methyl acrylate.

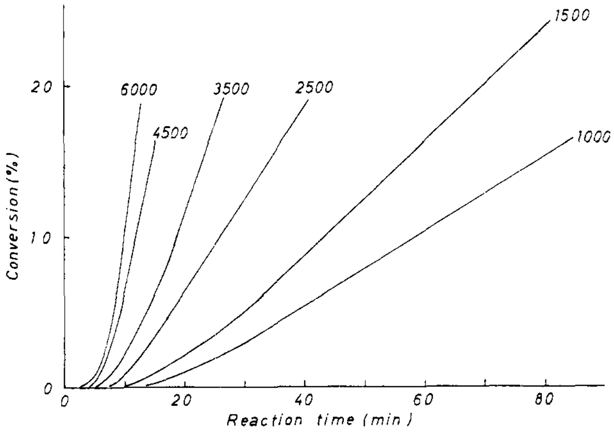

Figure 4. Typical time–conversion curves of vinyl acetate at various pressures and 20 °C.

can be considered that the planar methyl acetate molecule aligns with the CH_3–CO–O– group and the system goes from an isotropic (normal liquid) to an anisotropic liquid phase (mesophase) above the break pressure. Such a mesophase may be realized prior to crystallization because of inhibition of crystallization by rotation of the methyl group around the C–O bond (A).

Polymerization at High Pressure. Figure 4 shows typical time–conversion curves of vinyl acetate at 20 °C at various pressures. The polymerization rate accelerates at the initial stage and then becomes constant. The polymerization rate was defined from the slope in the steady state. Figure 5 shows the van't Hoff plot of the polymerization rate at 20 °C. The van't Hoff plot is regarded as smooth upon pressure. The smooth van't Hoff plot is exceptional in the polymerization of monomers that show the characteristic P–V relation. The activation volume is -9 cm^3/mol at the low-pressure side. The activation volume of vinyl acetate varies according to the polymerization system, such as bulk[15] and solution systems,[16] and was reported to be -7 to -17 cm^3/mol. The value obtained in this work is considered to be reasonable.

Difference in Vinyl Acetate and Methyl Acrylate. As reported recently,[9] the polymerization rate of methyl acrylate behaves characteristically in accordance with the discontinuous change in the P–V relations; the rate becomes a minimum at the pressure giving a break in the P–V isotherm (200 MPa at 20 °C), and the polymerization rate hardly depends on pressure in the pressure range 300–400 MPa at 20 °C. It is believed that the alignment of monomer molecules over a short range above the break pressure affects the propagation reaction, because mobility of vinyl group is lowered by the alignment. When the monomer molecules align mainly with the vinyl group, the rate of polymerization is not accelerated by compression for the same reason. These considerations support a concept from P–V–T relations that the monomer system turns to an anisotropic liquid phase with short-range order above the break pressure.

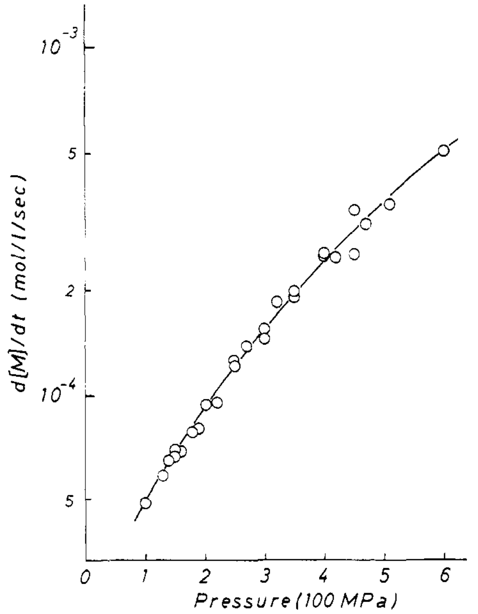

Figure 5. van't Hoff plot of polymerization rate of vinyl acetate at 20 °C.

In the case of vinyl acetate, a characteristic pressure dependence of the polymerization rate is not observed in spite of the occurrence of an isotropic-to-anisotropic liquid transition (from P–V data). The difference in the experimental results between methyl acrylate and vinyl acetate can be interpreted by their molecular structures. The molecules are structural isomers and the only difference in the structures is the position of the ether-bonding oxygen atom as shown in Figure 3. As seen in the figure, the =C–CO–O– and –O–CO–CH_3 groups are large, planar, and comparable with the vinyl group and the results in Figure 2 show that =C–CO–O– group can be aligned over a short range under suitable conditions. In the case of methyl acrylate, the geometry between the vinyl and =C–CO–O– groups is changed only by rotation on the bond (B); accordingly the freedom of mobility of one group is restricted when the other group aligns at high pressure. On the other hand, freedom of geometry between the vinyl and –O–CO–CH_3 group of vinyl acetate is larger than the one of methyl acetate, because the C–O–C group serves as a free rotative joint between the groups.

The comparison of the P–V and polymerization data leads to a conclusion that the geometry and freedom of mobility between two planar groups affect the mode of pressure-induced alignment, and the pressure dependence of the polymerization rate is affected mainly by the freedom of mobility of the vinyl group in the aligned monomer system. Most of the vinyl monomers measured by us show a discontinuous volume change above 40 °C, but in the case of vinyl acetate this characteristic volume change disappears. This is closely related to the freedom of mobility of both planar segments.

Registry No. Vinyl acetate, 108-05-4; methyl acetate, 79-20-9.

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Polydispersity Variation and the Polymer Self-Diffusion Exponent

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ABSTRACT: We establish a general method of modeling polydispersity, its variation, and its effects. As a sample application of our idea, we reevaluate polydispersity effects as they occur in a novel test of reptation theory, the forced Rayleigh light scattering experiment of Leger et al.[2] In their study of the polymer self-diffusion coefficient, the analysis of polydispersity effects relies on the use of first cumulants to give an approximate treatment of molecular weight distribution averages and completely neglects the effects of polydispersity *variation.* In light of our model, we find that this can be considerably improved, even for the low polydispersities employed in their experiment. In order to redetermine the implications of their results, we find that it is essential not only to accurately calculate the molecular weight average of the monodisperse diffusion coefficient but also to properly compute the predicted decay in the density of the flash-excited pattern. As in our earlier paper concerning the molecular weight dependence of the zero-shear-rate viscosity, we again emphasize the general concept that the *rate of change* of polydispersity is more important than the polydispersity itself, as far the careful determination of exponents occurring in power-law molecular weight relations is concerned. Our model of the effects of polydispersity variation can be adapted and applied to any other experimental program where the type of molecular weight averaging which enters is known.

I. Introduction

The fundamental nature and appealing simplicity of the reptation model of de Gennes[1] make its applicability to entangled polymeric systems an important question. Leger et al.[2] have recently studied polystyrene chains in semidilute solution in order to test the prediction of reptation theory that the self-diffusion coefficient varies with molecular weight according to

$$D(M) \propto M^{-2} \qquad (1.1)$$

Their experimental value for the self-diffusion coefficient exponent is quoted as 2 ± 0.1. This apparent confirmation of reptation theory contrasts with the problem of the zero-shear melt viscosity η, where several independent rheological studies[3-5] of the viscoelastic properties of polystyrene and other linear polymers seem to indicate an exponent of 3.4 in the power-law dependence of η on molecular weight. Reptation theory predicts an exponent of 3. In an earlier paper[6] we have found that this discrepancy cannot be explained away by polydispersity effects.

We have established a general approach to modeling the effects of polydispersity. The cornerstone of our method is to use a model molecular weight distribution to compute any required average over molecular weight. The first application of this simulation method was given in our preceding paper on the zero-shear viscosity. In the present paper we state our model and apply it to determine the nature and extent of these effects in self-diffusion coefficient studies.

When theory is compared with experiment, polydispersity effects always enter because actual measurements are performed on systems having a distribution of molecular weights. Although the very low polydispersities provided by fractionation and anionic polymerization can be taken advantage of to minimize the effects of molecular weight distribution, increasingly accurate experimental techniques justify and require the detailed examination of polydispersity effects even for systems of low polydispersity. The novel technique of forced Rayleigh light scattering employed by Leger et al. is a case in point, as we shall illustrate later in this paper.

There are two quite different aspects to the effects of polydispersity on the dynamics of concentrated polymeric systems. The first enters on the microscopic level and asks how the motions of a polymer chain are modified when the surrounding chains form a polydisperse medium rather than a monodisperse one. In the context of the original reptation model one could still claim that the chain only interacts with an averaged environment, specifically a confining tube. Therefore the molecular weight dependences derived for monodisperse systems would still be valid. Of course, this cannot be completely correct since the presence of very short chains probably reduces entanglement and reptation. At present there are no convincing extensions of the theory that address this question; the monodisperse relations are usually assumed.

The second aspect of polydispersity effects concerns the averaging over the molecular weight distribution when a macroscopic quantity is determined by the combined properties of the individual chains forming the distribution. The type of averaging that occurs seems obvious in some situations, but not at all in others. As an example of the latter, we consider the molecular weight dependence

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