catalytic reaction was entropy controlled.[23]

Cohen et al. suggested that α-chymotrypsin catalysis by desolvation of substrate in the neighborhood of hydrophobic residues of the enzyme molecule contributed a factor of 10^3 or so to the rate of catalysis.[24] Warshel also pointed out the importance of solvation energy on the energetics of enzymatic reactions.[25] Recently, we pointed out that "polymer catalysts" which provide reaction site in the polymer domain change reaction rates by solvation and/or desolvation of substrate and/or transition state.[10,18,26] The present work seems to corroborate these suggestions.

Registry No. OAA, 328-42-7; PEI, 9002-98-6; C_4PEI, 84680-84-2; C_8PEI, 84680-85-3; PLL, 25988-63-0; PLL, SRU, 26588-20-5; PB, 28728-55-4; butylamine, 109-73-9; Me_2SO, 67-68-5; decarboxylase, 9027-22-9.

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Determination of the Correlation between Molecular Weight Distribution and Chemical Composition Distribution in a High-Conversion Copolymer

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ABSTRACT: The dual distribution of molecular weight and chemical composition of a high-conversion copolymer was determined by combination of preparative gel permeation chromatography (GPC) and thin layer chromatography (TLC). A high-conversion statistical copolymer of styrene–methyl acrylate (S–MA) was separated into 11 fractions with respect to molecular weight by preparative GPC. The chemical composition distribution (CCD) of each fraction was determined by TLC. The three-dimensional distribution of molecular weight and chemical composition was constructed from those data. The CCD's of lower molecular weight fractions are not appreciably different from that of the original sample. Their CCD's have a main peak at a low MA content and a long tail toward the higher MA-content region. On the other hand, the CCD's of higher molecular weight fractions are shifted toward the higher MA-content region. These features of the dual distributions are well explained by analyzing two phenomena occurring simultaneously, i.e., the increase of molecular weight due to the so-called gel effect and the change of MA content with conversion.

Introduction

It is well-known that high-conversion copolymers have both molecular weight distribution (MWD) and chemical composition distribution (CCD) and a correlation exists between those two distributions. It is very important to know the correlation for the study of copolymerization kinetics and also for the study of the effect of MWD and CCD on physical properties of copolymers. Nevertheless, only a few papers dealing with the determination of the correlation have been published.[1-3]

By using an analytical GPC with dual detectors, we previously showed that a high-conversion copolymer of styrene (S) and methyl acrylate (MA) prepared in bulk has a broad MWD and the MA content of the fractions at point-by-point increases as the molecular weight (MW) increases.[4] The experimental data are reproduced in Figure 1. These facts were explained by the so-called gel effect in the copolymerization kinetics. That is, the MW of the components produced at high conversion is higher than that of the components produced at low conversion due to the gel effect, while the MA content of the components increases as the conversion increases. Consequently, a characteristic correlation is found between MW and chemical composition (CC) in high-conversion copolymers. However, this is simply a qualitative explanation.

In the present work, the dual distributions of MW and CC in a high-conversion sample of S–MA copolymer were determined by combination of a preparative GPC and TLC to confirm this explanation.

Experimental Section

Samples. The sample used in the present work is the same S–MA statistical copolymer (B-60) as used in our previous

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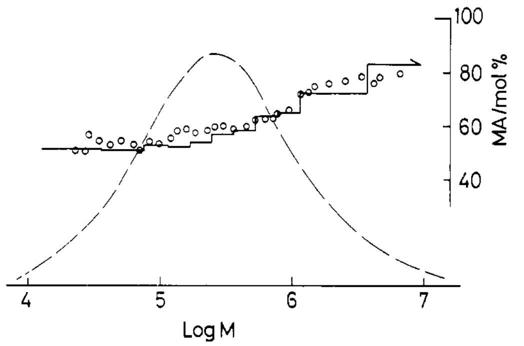

Figure 1. Relationship between average MA content and molecular weight of each fraction of sample B-60. The solid lines show the average MA content of each fraction by TLC (in this work). The circles show the average MA content point by point, and the broken line shows the overall molecular weight distribution by analytical GPC.[4]

works.[4-6] The sample was prepared by polymerizing a monomer mixture containing 60.0 mol % of MA to 92.0 wt % conversion in bulk. The average MA content of the sample was 56.4 mol % by elemental analysis and 56.1 mol % by ^{1}H NMR. The number-average molecular weight, M_n, was $4.8_2 \times 10^5$. The CCD of the high-conversion sample was determined by cross fractionation[5] and TLC.[6] Both results satisfactorily agreed with that calculated from the classical theory of copolymerization.

Low-conversion samples of N-45 (MA/mol % = 46.6), N-60 (57.3), and N-75 (77.9) and also a homopolymer of MA, PMA, were used as the reference samples for the TLC experiments. The fractions of the N-series samples obtained by molecular weight fractionation were used for determination of the intrinsic viscosity vs. MW relationship. The procedures of the preparation, fractionation, and characterization of the samples were described in a previous paper.[4]

The monodisperse polystyrenes supplied from the National Bureau of Standards (U.S.A.) and Toyo Soda Manufacturing Co., Ltd. in Japan were used as the standard samples for the universal calibration of GPC.

Solvents of the reagent grade were purified by the following ways: Chloroform was dried with $CaCl_2$ and distilled fractionally. Carbon tetrachloride was refluxed with an aqueous solution of NaOH (10%) for about 3 h, washed with water several times, dried with $CaCl_2$, and fractionally distilled. Methyl acetate was distilled fractionally after drying with $MgSO_4$. Methanol was simply distilled.

Intrinsic Viscosity, Molecular Weight Determinations, and Analytical GPC. The intrinsic viscosities, $[\eta]$'s, of the copolymer samples and also of the standard polystyrenes were determined in chloroform at 30 °C by using a viscometer of the Ubbelohde type with negligible kinetic energy correction. The M_n's of the copolymer samples and their fractions were determined by membrane osmometry as in the previous work.[4] The MW's of the standard polystyrenes were given by the suppliers. Analytical GPC of the copolymer samples was carried out by using dual detectors as in the previous work.[4]

Preparative GPC. Preparative GPC of a copolymer sample (B-60) was carried out by a high-speed liquid chromatography, HLC-802R of Toyo Soda Manufacturing Co., Ltd. The column set was composed of two prepacked columns of TSK-GEL, GMH-G6, with a length of 60 cm and a inner diameter of 2.5 cm. The theoretical plate number of the column set was 2.4×10^4. The fractionation of the sample was carried out in chloroform degassed by ultrasonic waves just before use at the flow rate of 5.0 mL min^{-1}, 30 °C. The copolymer concentration of the sample solution injected was 0.5 g dL^{-1} and the injection volume was 2.0 mL.

In chloroform, the elution volume, V_e, of the present copolymer is practically unaffected by CC but is determined by MW only. The viscosity equation of the copolymer in this solvent is also approximately expressed by a common equation irrespective of CC, as shown in the later section. Therefore, it is certain that the fractionation by GPC in chloroform occurs with respect to MW only.

The copolymer sample was separated into 11 fractions with a fraction collector. The volume intervals in the fractionation were 30 mL for fraction 1, 15 mL for 2, 5 mL for 3–9, 10 mL for 10, and 25 mL for 11, respectively. The fractionation was repeated 100 times. The fractions at the same elution volume were combined. The combined solutions were concentrated by a rotary evaporator and poured into a large excess of methanol. The copolymer fraction, thus precipitated, was washed with methanol several times and dried in vacuo until a constant weight was attained.

The universal calibration curve for GPC was obtained by plotting log ($M[\eta]$) against V_e for the standard monodisperse polystyrenes. GPC of the standard samples was carried out under the same experimental conditions as in the preparative GPC of the copolymer sample, except that GPC of the standard samples was carried out at 0.1 g dL^{-1}. The peak heights of the standard samples at that concentration were nearly equal to the height of the copolymer sample at 0.5 g mL^{-1} in the preparative GPC.

V_e for the copolymer sample can be converted to $M[\eta]$ by use of the universal calibration curve thus determined, and then to M by use of the M–$[\eta]$ relationship of the copolymer.

Determination of the M–$[\eta]$ Relationship of the Copolymer. The double logarithmic plot of $[\eta]$ in chloroform at 30 °C vs. M_n was carried out for the several fractions of N-series copolymer samples. All the data points approximately fit a common straight line irrespective of CC's of the fractions, as was found in THF in the previous work.[4] The common viscosity equation obtained by the least-squares method is

$$[\eta] = (1.41 \times 10^{-4})M_n^{0.75} \quad (\text{dL g}^{-1}) \tag{1}$$

The copolymer fractions used to determine this relationship were not completely monodisperse with respect to MW. The value of K (in $[\eta] = KM^{\nu}$) for monodisperse fractions should be used for the present purpose. It was found, in previous work,[4] that M_w/M_n of the present fractions is about 1.25, and hence the ratio of the K value for the present fractions to the value for the monodisperse samples (K_n/K) should be 1.18. The viscosity equation calibrated by using the value of K_n/K is

$$[\eta] = (1.19 \times 10^{-4})M^{0.75} \quad (\text{dL g}^{-1}) \tag{2}$$

Determination of CCD by TLC. The CCD's of the copolymer fractions obtained by the preparative GPC were determined by a TLC method. Precoated plates of silica gel (Analtech Uniplate Silicagel GH-2511) were used as the adsorbent layer. The copolymer samples of 20 μg were deposited on the layer from their chloroform solutions of 2 μg μL^{-1}, together with the reference samples. The concentration gradient development was applied by using a mixture of CCl_4 and methyl acetate as the eluent, according to Inagaki et al.[7] The methyl acetate content was linearly increased from 6.0 to 43.0 vol %. The visualization of the polymers was carried out by spraying sulfuric acid and heating the chromatoplate. The chromatogram of blackness as a function of migration distance was determined by using a Shimazu high-speed chromatoscanner, Model CS-920 (Shimazu Seisakusho Co., Japan). In the previous work,[6] the reproducibility of the chromatogram area (blackness) was examined for 16 spots of the respective reference samples containing the same amount of the polymers (10 μg). The relative standard deviation was 6.8% for 64 spots, if the spraying and the heating were sufficient. Further details of the TLC experiments and the procedure of the determination of CCD from the chromatogram were described in the previous paper.[6]

Results

The recovery of the sample in the GPC fractionation was 94.8 wt %. The weight fraction, the MW range, and the average MA content of the respective fractions are summarized in Table I. The average MA content of the whole sample, calculated from the data, is 59.4 mol %, which is close to the value of the original sample, considering the accuracy of the TLC method.

The three-dimensional distribution of CC and MW is illustrated in Figure 2 by plotting the CCD of each fraction

Table I
Results of Fractionation by Preparative GPC

fraction	range of MW × 10^{-4}	fraction weight	MA content, mol %[a]
1	>370	0.0527	83.4
2	370-113	0.1129	72.6
3	113-78	0.0681	65.1
4	78-53	0.0869	64.0
5	53-36.5	0.1041	58.8
6	36.5-24.7	0.1132	57.2
7	24.7-16.8	0.1109	54.2
8	16.8-11.3	0.0989	52.5
9	11.3-7.8	0.0806	52.6
10	7.8-3.6	0.1064	51.1
11	3.6-0	0.0655	51.7
			av 59.4

[a] Average values calculated from CCD by TLC.

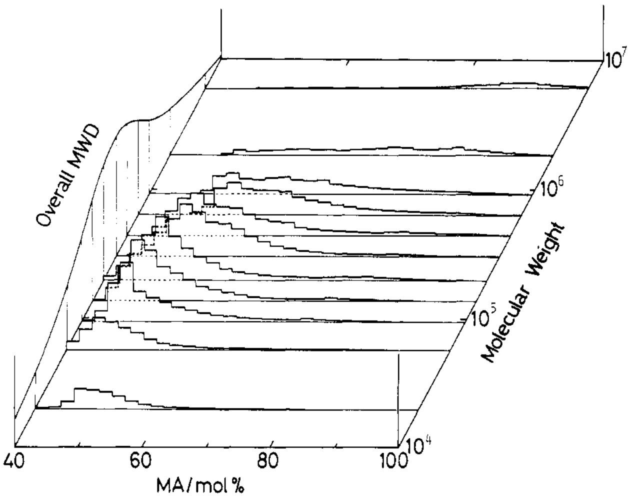

Figure 2. Three-dimensional distribution of chemical composition and molecular weight of sample B-60.

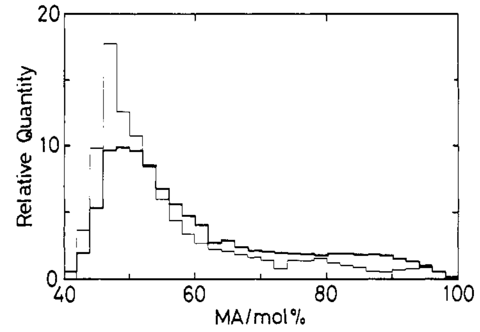

Figure 3. Overall chemical composition distribution curve of sample B-60. The thick line shows the overall chemical composition distribution curve composed by accumulating the CCD's of the respective fractions (this work). The thin line shows the overall chemical composition distribution curve of the whole copolymer obtained in previous work.[6]

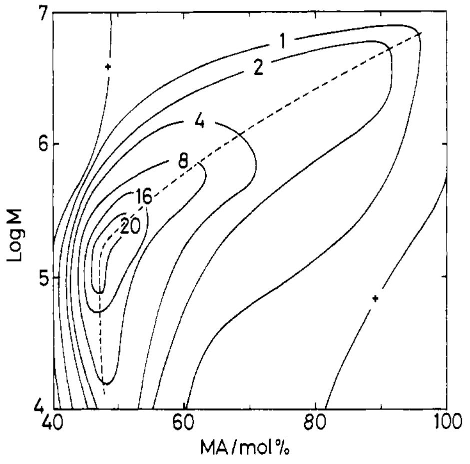

Figure 4. Schematic contour line map of the three-dimensional distribution of chemical composition and molecular weight. The numerals show the relative heights. The marks (+) show the boundary lines inside which the copolymer components are detected.

perpendicularly over the straight line presenting a constant MW. The MW is the value at the center of gravity in the MWD of the fraction. The center of gravity was determined taking into account the MWD of this sample determined in the previous work.[4] The height of each CCD curve is determined in proportion to the height of the MWD curve at the MW.

The average MA content of each fraction in Table I, calculated from the CCD of the fraction, is shown by solid lines in Figure 1, for comparison with the results obtained by an analytical GPC with dual detectors.[4] Variations of MA content with MW in both experiments are in good agreement with each other.

The overall CCD was composed by accumulating the CCD's of the respective fractions. In Figure 3, the overall CCD thus composed is compared with the CCD of the whole copolymer determined by TLC in the previous work.[6] Although the composed CCD is somewhat broader than that of the whole copolymer, the agreement between two CCD's is satisfactory.

Discussion

The dual distribution of MW and CC of this high-conversion copolymer was fully characterized in Figure 2. The CCD's of lower MW fractions are not appreciably different from the CCD of the original sample. Both have a main peak at a low MA-content region (46–48 mol %) and a long tail toward the higher MA-content region. On the other hand, the CCD's of higher MW fractions are shifted toward the higher MA-content region. Moreover, the CCD diffuses and becomes much wider in the middle MW fractions. Then, the CCD of the highest MW fraction becomes again narrower than those of the middle fractions. The fraction does not contain the components corresponding to the main peak in the CCD of the original sample.

Such features in the dual distributions of MW and CC may be understood more easily from a schematic contour line map shown in Figure 4, which was constructed from the data in Figure 2. The ridge of the three-dimensional surface is shown by a dashed line in the figure. In the region of lower MW, the ridge is parallel to the MW axis, but turns toward the higher MA content in the region of higher MW. That is, the correlation between MW and CC becomes characteristic beyond the turning point of the ridge. Moreover, in both regions of very high MW and low MA content and of very low MW and high MA content, the copolymer components cannot be detected.

It is well-known as the gel effect[8] in polymerization kinetics that if the polymerization is continued to a high conversion, the rate of the termination reaction may be reduced due to the increasing viscosity of the polymerization mixture, and, consequently, the MW of the components produced increases with conversion. On the other hand, the MA content of the components is not affected by the gel effect but is controlled only by the propagation reaction. Therefore, the CC of the components drifts toward the higher MA content as the conversion increases. From these two phenomena occurring simultaneously, we 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, $f_{\mathrm{MA}}{}^0 = 0.60$, and the monomer reactivity ratios, $r_{\mathrm{MA}} = 0.18$ and $r_{\mathrm{S}} = 0.75$.[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