Preparation and Characterization of a Star-Shaped Polymer

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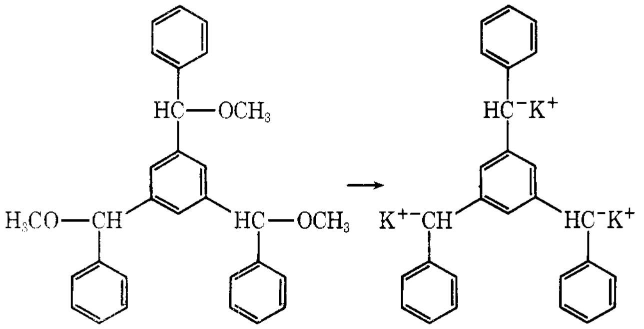
ABSTRACT: To prepare star-shaped polymers having long branches at high purity, α-methylstyrene was polymerized with a trifunctional anionic initiator in THF at −78 °C. The polymerization products contained one- and two-branched (linear) polymers in addition to the star-shaped polymer. They were fractionated by elution chromatography. It was confirmed that those three components have molecular weights in the ratio of 1:2:3. The highest molecular weight of a branch was beyond 1×10^6.

Various methods[1-12] have been reported for preparing star-shaped polymers. The study of physical properties of branched polymers may be one of the current topics in polymer science, not only because of the practical importance of branched polymers but also because of their importance in examining the basic theories in polymer science. The samples required for the study should have well-defined structures and high purities. Moreover, it is also important that the branches are long enough for measurement of radius of gyration or for entanglement formation in concentrated solutions. The method we would like to report here is an anionic polymerization with a trifunctional initiator which was first suggested by Szwarc[13] and reported by Asami.[14] By this method we obtained star-shaped samples with long branches at high purities.

Experimental Section

Monomer, Solvents, and the Other Chemicals. The α-methylstyrene monomer and solvents such as tetrahydrofuran (THF), diglyme, etc., were purified in such ways as reported previously.[15] The monofunctional initiators such as n-butyllithium and cumylpotassium were also prepared by the methods reported previously.[16] The other chemicals used for preparation were of the first grade of Katayama Chemical Co. and were without purification.

Preparation of Trifunctional Initiator. Various kinds of mutifunctional compounds were reacted with alkali metals or sodium–potassium alloy to make multifunctional anionic initiators. Among them, 1,3,5-tris(α-methoxybenzyl)benzene (TMBB), which was first reported by Asami,[14] was most successful.



The potassium content of the initiator solution was determined by titration with a standard HCl solution. The weight concentration of the initiator solution was estimated from the amount of TMBB used. The degree of contamination of the initiator by Na^+ was determined by an atomic absorption spectrophotometer Hitachi 207.

Polymerization. The polymerization of α-methylstyrene with the trifunctional initiator was carried out in the same way as with monofunctional initiators.[15] The initiator was added to the mixture of THF and monomer at room temperature and the polymerization was started by dipping the glass flask in a dry ice–acetone bath. The polymerization was stopped by pouring the mixture into methanol. However, the cleaning of the glass apparatus and others was done much more carefully than in the polymerization with monofunctional initiators to increase the yield of the star-shaped sample.

Determination of Yield. Determination of the yields of the star-shaped and the other components in the polymerization products was carried out by sedimentation method, using a Beckman Model E or Hitachi Model 1-A. The sedimentation coefficients of branched polymers were calculated by Stockmayer and Fixman[17] and also by Kurata and Fukatsu[18] using the theory of Kirkwood[19] on the translational frictional coefficient of polymers in solution. The ratio of the sedimentation coefficient of a star-shaped polymer (S^0) to that of a corresponding linear polymer having the same molecular weight (S^0_l) at the Θ temperature is given by

$$S^0/S^0_l = [2 - f + 2^{1/2}(f - 1)]/f^{1/2} \qquad (1)$$

where f is the degree of branching. Moreover, the ratio of the sedimentation coefficient of the linear polymer to that of the branch molecule (S^0_b) is

$$S^0_l/S^0_b = f^{1/2} \qquad (2)$$

From eq 1 and 2 we have

$$S^0/S^0_b = (2^{1/2} - 1)(f + 2^{1/2}) \qquad (3)$$

Thus, the ratios of the sedimentation coefficients of three- and two-branched polymers to that of a branch molecule in Θ solvents (i.e., $S^0(f = 3)/S^0_b$ and $S^0(f = 2)/S^0_b$) are 1.82 and 1.41, respectively. The relationship between sedimentation coefficient and molecular weight of monodisperse linear poly-α-methylstyrenes in cyclohexane at 35 °C (Θ temperature) is[20]

$$S^0_l = 1.8 \times 10^{-15}\, M^{1/2} \qquad (4)$$

Therefore, the assignment of peaks can be made by comparing the observed sedimentation coefficients with these calculated values. The amount of each component in the polymerization product may be determined from the corresponding peak area neglecting a correction for the Johnston–Ogston effect.[21]

Fractionation. The polymerization product was first fractionated by a precipitation fractionation method using a benzene–methanol system to increase the content of the star-shaped polymer up to about 70%. It was found practically impossible to isolate the star-shaped polymer only by the precipitation–fractionation method.

The sample rich in the star-shaped polymer was further fractionated by elution chromatography using a stainless steel column of 1800-mm length, 60-mm inner diameter, and 5087-cm³ volume. Glass beads of 100–200 and 200–300 mesh were packed in the lower and upper parts of the column, respectively. The hold-up volume was 1880 cm³. The temperature of the column was kept at constant by circulating a constant temperature water in the outer jacket. The fluctuation of temperature in the column was found to be within ±0.01 °C when measured with thermocouples inserted into the column. About 15 g of the sample was dissolved in cyclohexane at 45–50 °C and transferred into the column from the top of the column. The sample was deposited on the beads in the lower part of the column by lowering the temperature to about 10 °C. The components with one and two branches were first eluted out by circulating a large amount of cyclohexane from the bottom to the top of the column at a constant temperature. The temperature was increased stepwise and the elution was repeated. The final elution was carried out at a temperature a little below the precipitation temperature of the component with two branches. The concentration of the elute was very low and the flow rate of cyclohexane was 100–400 mL/h. After a considerable part of the polymer was eluted out, the sample remaining on the glass beads was found to be the pure star-shaped polymer.

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The solution in each fraction was concentrated by distillation under reduced pressure and benzene was added to the solution. The solution was filtered through a 10 μm millipore filter and freeze-dried. The yield was about 2–3 g. About a week was necessary for a cycle of elution.

Molecular Weight Determination. The number and weight average molecular weights of the components were determined by osmometry and light scattering, using a Hewlett Packard High Speed Membrane Osmometer 502 and a modified Shimadzu light-scattering photometer or Fica 50, respectively. The measurements were carried out in cyclohexane at 35 °C or in toluene.

The intrinsic viscosity was determined by capillary viscometers of the Ubbelohde type. The relationship between the intrinsic viscosity $[\eta]$ and the weight average molecular weight of linear poly-α-methylstyrenes in cyclohexane at 35 °C is[22]

$$[\eta] = 6.7 \times 10^{-4}\, M^{0.50} \qquad (5)$$

Results

Initiator. 1,3,5-Tris(benzyl)benzene (36 g) was dissolved in 300 mL of ethanol. The solution was refluxed with 10 g of sodium borohydride for 3 h. The color of the solution became brown. Sodium borohydride remaining unreactive was decomposed with addition of an aqueous solution of acetic acid and ethanol was evaporated from the mixture. A 50% aqueous solution of acetic acid was added to the residue and heated to 60–70 °C for 2 h. The 1,3,5-tris(α-hydroxybenzyl)benzene produced was filtered and recrystallized in the MEK–*n*-hexane system: yield 88%; mp 173–174 °C. 1,3,5-Tris(α-hydroxybenzyl)benzene (30 g) thus prepared was dissolved in 1000 mL of methanol. HCl gas was bubbled into the solution at 15 °C and kept at the temperature for 3 h. Alchol and HCl were extracted with ether. The product, 1,3,5-tris(α-methoxybenzyl)benzene (TMBB), was distilled under high vacuum twice: bp 220–222 °C (2×10^{-5} mmHg); NMR (CCl_4) τ 6.73 (s, 3 H, OCH_3), 4.90 (s, 1 H, CH), 2.88 (s, 5 H, C_6H_5).

THF solution of TMBB was reacted with sodium and potassium alloy in vacuo to be converted to the corresponding three-functional anionic initiator in an apparatus as shown in Figure 1. First, THF solution of a sample, sodium–potassium alloy, and THF containing a small amount of cumylpotassium were enclosed in vacuo in flasks W, S, and Z, respectively. After the whole apparatus was evacuated to 10^{-6} mmHg, the apparatus was sealed off and the sodium–potassium alloy in S and THF in Z were transfered into a reaction vessel V. The whole apparatus was washed well with the THF solution of cumylpotassium and the solution was transfered to flask X. THF in X was distilled into V and was again used to wash the apparatus. By repeating this procedure, all impurities and a small amount of the remaining cumylpotassium was collected in X, and clean sodium–potassium alloy and THF were left in V. The flask X was sealed off.

THF solutions of TMBB in W were transferred into V to be reacted with sodium–potassium alloy in THF. Stirring of the mixture was continued at room temperature for 5–7 h. Some preliminary experiments showed that the reaction was insensitive to temperature. The colored solution thus obtained was filtered through a glass filter F into flask I and sealed off.

The K^+ content of the multicarbanion thus produced was approximately three per molecule as expected. The degree of contamination by Na^+ was 0.1–0.2%. However, the initiator appears to be unstable even in a refrigerator. The color disappeared and a fairly large amount of precipitant appeared in ampules in a week at −25 °C. The initiator can be stabilized by addition of an electrolyte such as potassium ethoxide since electrostatic repulsion between charged groups is suppressed. A kind of complex may be formed between the anionic group and potassium ethoxide. Instead, however, the initiator has little ability to produce the star-shaped polymer but produces only one- and two-branched polymers. It was confirmed by many experiments that the initiator solution containing potassium methoxide which passed through the coarse glass filter F in Figure 1 cannot produce the star-shaped polymer, whereas the same initiator can produce the star-shaped polymer if the potassium methoxide is removed by addition of *n*-hexane. The reason for the effect of added alcoholates on the initiation ability of the initiator cannot be clarified in this work, but the same phenomenon was found in the polymerization of α-methylstyrene with *n*-butyllithium.[15]

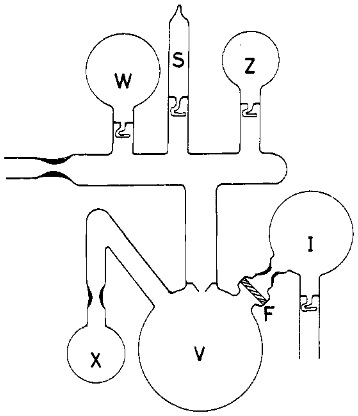

Figure 1. The apparatus for preparation of multifunctional initiator.

Just before use of the initiator, therefore, the alcoholate was precipitated by addition of *n*-hexane and the initiator solution free of alcoholates was obtained by decantation. The appropriate volume ratio of *n*-hexane to THF may be approximately 3:10.

Polymerization. Even with this purified initiator, no star-shaped polymers are obtained if the polymerization is carried out in pure THF. This may be because the ionization of the third group is suppressed by an electrostatic effect of the ionized groups. If the dissociation of potassium ion is increased by addition of diglyme to the solvent, the yield of the star-shaped polymer can be increased considerably. An example of the sedimentation pattern of the polymerization products is shown in Figure 2.

To eliminate the pressure effect, the sedimentation coefficients of three peaks were extrapolated to the meniscus using the equation of Fujita.[22] Figure 3 shows the plot of the apparent sedimentation coefficient against $(x_a/x_m)^2 - 1$ where x_a and x_m denote the positions of the maximum and the meniscus, respectively. The initial time was determined by the method of Elias.[23] The sedimentation coefficients of three components obtained by extrapolation to the meniscus are 1.79_5, 1.46, and 1.07×10^{-12} s, respectively, and the ratios of those values are $S^0(f = 3)/S^0{}_b = 1.66$ and $S^0(f = 2)/S^0{}_b = 1.36$. The observed values are a little lower than the theoretical values. Considering the concentration dependence of sedimentation coefficient and the other ambiguities concerning the sedimentation coefficient of branched polymers, however, it may be concluded that three peaks correspond to the three-, two- and one-branched components, respectively. The yields of three components can be calculated from the peak area.

The yields of components in polymerization products obtained at various conditions are summarized in Table I. In some experiments such as A-1 and A-2, where the yields of total polymers are low, the polymerization was stopped in the middle. In all experiments, no tendency of deactivation of the initiator was observed. From those experimental results it was concluded that the effect of diglyme increases with increasing concentration but reaches a maximum at about 7%.

Even if a large enough amount of diglyme is contained in THF, moreover, the relative yields of each component depend

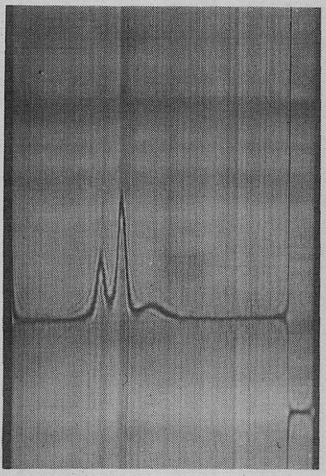

Figure 2. An example of the patterns of polymerization products of sample No. S-20: solvent, cyclohexane; 35 °C; concentration, 0.55%; 58780 rpm.

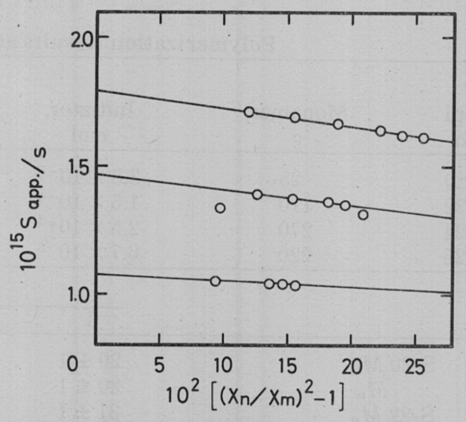

Figure 3. Extrapolation of the apparent sedimentation coefficient to one atomic pressure. The data show the apparent sedimentation coefficients of three-, two-, and one-branched polymers from top to bottom, respectively. Sample No. A-2: solvent, cyclohexane; 35 °C; concentration, 0.1089 g/dL; 59780 rpm.

on the ratio of monomer and initiator. In Figure 4, the relative yields of three components, obtained in the presence of a large enough amount of diglyme (>7%), are plotted against the ratio [M]/[I]. The larger the ratio [M]/[I] is the higher the yield of star-shaped polymer would be. The experiments in Table II were carried out at a high ratio of [M]/[I] and also at larger scales of polymerization. The yield of star-shaped polymer increased as speculated. However, reproducibility of the experimental results was very poor probably because of unrevealed errors arising from increasing the polymerization volume. The highest yield of star-shaped polymer by this method was about 35%.

The experimental results in Figure 4 can be quantitatively explained if we assume that the ion pair cannot initiate the polymerization and the monomer takes part in the dissociation equilibrium of ion pairs. However, we cannot discuss this problem at the present stage.

Fractionation and Characterization. Polymerization products were fractionated into three components and the purities of the samples fractionated were examined by sedimentation. An example of the sedimentation patterns of fractionated samples is shown in Figure 5. It is clear that neither one- nor two-branched polymers are contained in the star-shaped polymer. The sample was further carefully pu-

Table I
Polymerization Results of α-Methylstyrene with the Three-Functional Initiator (solvent THF, temperature −78 °C)

Expt. No.	Monomer concn. [M], mol/L	Initiator concn [I], mol/L	[M]/[I]	Solvent, mL THF	Solvent, mL Diglyme	Solvent, mL Et_2O	Polymerization time, h
A-1	0.949	2.0×10^{-4}	$4.7_5 \times 10^3$	261	0	0	45.5
A-2[a]	1.58	2.8×10^{-4}	$5.6_1 \times 10^3$	86	10	0	1.33
A-3[a]	0.59_5	$3.4_5 \times 10^{-4}$	$1.7_3 \times 10^3$	36.6	6.7	0	8
A-4	0.59_5			39.7	7.2	0	9
A-5[b]	2.00	$3.0_2 \times 10^{-4}$	$6.6_4 \times 10^3$	51.9	9.0	0	1.75
B-1[a]	0.502	$8.0_3 \times 10^{-4}$	$7.4_0 \times 10^2$	40.8	7.4_5	0	17
B-2[c]	0.556	$1.8_8 \times 10^{-4}$	$2.9_1 \times 10^3$	31.9	5.8_3	0	9
B-3[a]	0.584	$3.9_8 \times 10^{-4}$	$1.4_9 \times 10^3$	37.7	6.8_9	0	13
B-4[a]	0.56_6	$2.2_7 \times 10^{-4}$	$2.5_9 \times 10^3$	41.5	10.9	0	9.5
B-5[a]	0.66_0	$3.6_2 \times 10^{-4}$	$1.8_2 \times 10^3$	32.4	5.6	26	15.5
B-6	1.29_7	$2.8_7 \times 10^{-4}$	$4.5_1 \times 10^3$	129	2.2	0	4.5
B-7	0.765	$1.8_7 \times 10^{-4}$	$4.1_0 \times 10^3$	45	1.8	0	11

Expt. No.	Total polymer yield, %	Rel yields of components (wt %) at branch No. 1	2	3	4
A-1	26.2	100	0	0	0
A-2	41.9	$23._9$	$50._2$	$25._8$	0
A-3	94.3	$50._3$	$49._7$	0	0
A-4	95<	$58._8$	$41._2$	0	0
A-5	30.3	$60._6$	$28._9$	$10._5$	0
B-1	95<	$70._9$	$29._2$	0	0
B-2	71.5	$57._8$	$42._3$	0	0
B-3	95<	$57._5$	$42._5$	0	0
B-4	95<	$45._5$	$54._5$	0	0
B-5	91	50	50	0	0
B-6	28.7	81	19	0	0
B-7	96.4	$65._7$	$34._3$	0	0

[a] These data are plotted in Figure 4. [b] The experimental data are unusual probably because of a too high concentration of monomer. [c] The experimental data are unusual probably because of a too low concentration of initiator.

Table II
Polymerization Results at a High Ratio of [M]/[I] and at Larger Scales

Expt No.	Monomer, g	Initiator, mol	THF, mL	Diglyme, mL	Polymer Yield Total, g	Polymer Yield Star content, %
S-20	25	3.8×10^{-5}	190	30	21	35
S-22	110	1.5×10^{-4}	800	25	91	12
S-24	270	2.5×10^{-4}	1800	300	160	11
S-26	220	6.7×10^{-5}	1800	250	92	12

	Mol wt of the components ($\times 10^{-4}$) at branch No. 1	2	3
S-20 M_n	29 ± 1	58 ± 2	87 ± 4
M_w	30 ± 1	58 ± 2	88 ± 3
S-22 M_n	31 ± 1	53 ± 2	90 ± 4
M_w			90 ± 5
S-24 M_w			116 ± 3
S-26 M_n[a]	117		
M_w			357 ± 10

[a] Calculated from $[\eta] = 7.3 \times 10^{-4}\ M^{0.50}$ in cyclohexane at 35 °C.

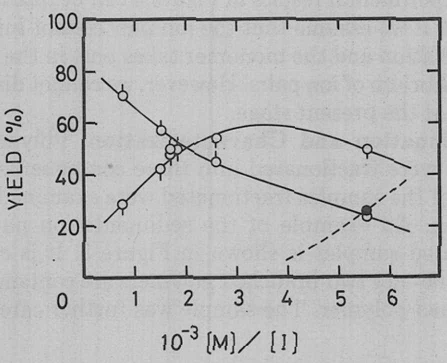

Figure 4. Yields of the one- (ȯ), two- (♀), and three-branched (●) polymers in polymerization products in mixed solvents of THF and diglyme. (Concentration of diglyme is over 7%.)

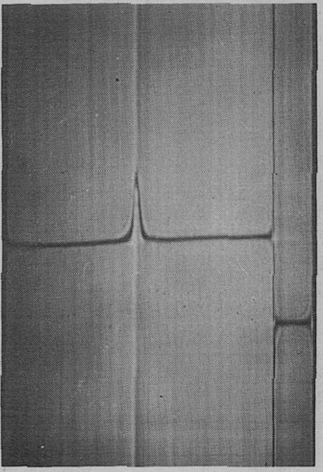

Figure 5. Sedimentation pattern of a star-shaped polymer. Sample No. S-22: solvent, cyclohexane; 35 °C; concentration, 0.15%.

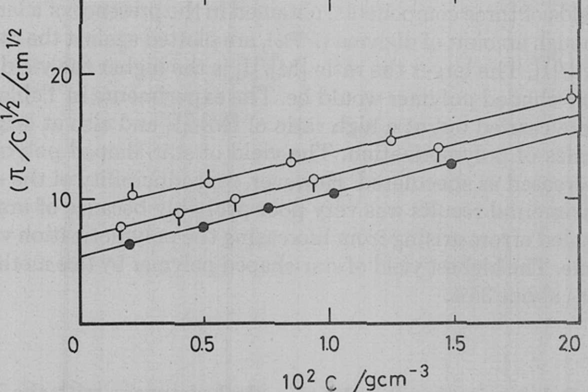

Figure 6. Square root of reduced osmotic pressure vs. concentration plots of three fractionated components in sample No. S-22: solvent, toluene; 25 °C. The graphs from top to bottom show the data for one- (ȯ), two- (♀), and three-branched (●) polymers, respectively.

rified by precipitation–fractionation method for characterization.

The number and weight average molecular weights of three components thus fractionated are summarized in Table II. The ratio of the weight and number average molecular weights, M_w/M_n, is close to unity. This result and the sedimentation patterns, such as Figure 2, show that the molecular weight distributions of these fractions are very sharp. Moreover, all data in Table II show that the molecular weights of three components in a polymerization product are in the ratio of 1.0:2.0:3.0, as expected. Examples of the square root of reduced osmotic pressure vs. concentration plots of three fractionated components are shown in Figure 6.

Discussion

Various preparation methods[1–12] of three or more branched polymers by coupling reactions between active chain ends and coupling agents were reported in the literature. We tried some of those methods. Since the concentration of active chain ends becomes very low, however, we could not have samples with long branches by these coupling methods. The highest molecular weight of a branch in star-shaped polymers prepared by coupling methods is about 3.5×10^5.[3,5,9,11]

It was really difficult to fractionate the polymerization product into pure components. The precipitation temperatures of three-branched (star) and two-branched polymers are very close if their molecular weights are high. We found it practically impossible to carry out the fractionation by the precipitation–fractionation method only. Even with the θ column, the isolation of star-shaped polymer was not successful if the temperature of cyclohexane was set at a temperature between the precipitation temperatures of two- and three-branched polymers. It was reported[24] that GPC with too high theoretical plates is required to observe two- and three-branched polymers separately. To have a star-shaped polymer at high purity, therefore, it is essential that the molecular weight distributions of the components in a polymerization product are so sharp that their purities after fractionation can well be confirmed by sedimentation.

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References and Notes

(1) M. Morton, T. E. Helminiak, S. P. Gadkary, and F. Bueche, *J. Polym. Sci.*, **57**, 471 (1962).
(2) T. A. Orofino and F. Wenger, *J. Phys. Chem.*, **67**, 566 (1963).
(3) T. Altares, Jr., D. P. Wyman, V. R. Allen, and K. Meyersen, *J. Polym. Sci. Part A*, **3**, 4131 (1965).
(4) S. P. S. Yen, *Makromol. Chem.*, **81**, 152 (1965).
(5) R. P. Zelinski and C. F. Wofford, *J. Polym. Sci. Part A*, **3**, 93 (1965).
(6) J. A. Gervasi and A. B. Gosnell, *J. Polym. Sci. Part A-1*, **4**, 1391 (1966).
(7) D. J. Worsfold, J. G. Zilliox, and P. Rempp, *Can. J. Chem.*, **47**, 3379 (1969).
(8) J. C. Meunier and R. Van Leempat, *Makromol. Chem.*, **142**, 1 (1971).
(9) (a) T. Masuda, Y. Ohta and Y. Onogi, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **12** (1), 346 (1971); (b) T. Masuda, Y. Ohta, and S. Onogi, *Macromolecules*, **4**, 763 (1971).
(10) J. Herz and C. Strazielle, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 747 (1971).
(11) J. E. L. Roovers and S. Bywater, *Macromolecules*, **5**, 384 (1972).
(12) J. E. L. Roovers and S. Bywater, *Macromolecules*, **7**, 443 (1974).
(13) M. Szwarc "Carbanions, Living Polymer and Electron Transfer Processes", Interscience, New York, N.Y., 1968.
(14) R. Asami et al., Presented at the 18th Symposium on Macromolecules, Japan 1969.
(15) T. Fujimoto, N. Ozaki, and M. Nagasawa, *J. Polym. Sci., Part A*, **3**, 2259 (1965).
(16) B. Ziegler and M. Schenell, *Justus Liebigs Ann. Chem.*, **437**, 255 (1924).
(17) W. H. Stockmayer and M. Fixman, *Ann. N.Y. Acad. Sci.*, **57**, 334 (1953).
(18) M. Kurata and M. Fukatsu, *J. Chem. Phys.*, **41**, 2934 (1964).
(19) J. G. Kirkwood, *J. Polym. Sci.*, **12**, 1 (1953).
(20) K. Mizutani, Master's thesis in Nagoya University, 1970.
(21) H. Fujita, "Foundations of Ultra-Centrifugal Analysis", Wiley, New York, N.Y., 1975.
(22) T. Kato, K. Miyaso, I. Noda, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 777 (1970); I. Noda, K. Mizutani, T. Kato, T. Fijimoto, and M. Nagasawa, *ibid.*, **3**, 787 (1970).
(23) H. G. Elias, *Makromol. Chem.*, **24**, 30 (1959).
(24) Y. Kato, T. Hashimoto, T. Fujimoto, and M. Nagasawa, *J. Polym. Sci.*, **13**, 1849 (1975).

Instantaneous Shape and Segmental Density of Flexible Linear Macromolecules. 3. Partly Iodized Polystyrene in Untagged Polystyrene

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ABSTRACT: In this work it is shown that when individual partly iodized polystyrene (IPS) molecules are suspended as a solid solution in a polystyrene (PS) matrix they are irregular in shape and possess a gross segmental density intermediate between uniform and Gaussian upon which fluctuations of the order of 100–200 Å in size are superimposed. At the same time they maintain their unperturbed radius of gyration. When the IPS molecules separate from the PS matrix, individually or as aggregates, they collapse in size while their density increases.

In the two previous papers of this series we have demonstrated that when no phase separation takes place, individual macromolecules of tagged poly-*cis*-isoprene (PIP) in untagged PIP[1] and tagged PIP in a polyisobutylene (PIB) matrix[2] possess neither spherical symmetry nor symmetrical or monotonically increasing segmental distribution density upon progressing from the molecular perimeter to its center. In both instances the instantaneous shape of the tagged PIP molecules was irregular. Internally, the segmental distribution appears as an association of high-density regions intermixed with regions of lower segmental density. The high-density regions tend, on the average, to be closer to the geometrical center of the macromolecule. Oftentimes an apron of low-density material extends out at the molecular periphery. It is obvious that when averaged over all angles and/or a large population of observable molecules, the shape and segmental density of the molecules become spherical and Gaussian.

In this work we use partly iodized polystyrene (IPS) molecules suspended in polystyrene (PS) matrix to determine whether the characteristics observed previously in PIP show also in other polymers.

Experimental Section

All solvents were reagent grade or better. They were distilled and kept over molecular sieves. Bromoform was kept in the dark. Polystyrene (PS) of $M = 2 \times 10^6$ and $M_w/M_n \leq 1.3$ was obtained from Pressure Chemical Co. (Lot 14b). Partial iodination of PS, exclusively in the para position, was performed according to the procedure of Braun.[3] For this work, the PS was iodized to the extent of 27 wt % (about half the rings are substituted) and used as such. In all preparations only PS of $M = 2 \times 10^6$ and the partly iodized PS (IPS) originating from such PS were used.

Samples for electron microscopy were prepared in the following manner: Mixtures containing 0.5, 1, 5, and 10% by weight of IPS in PS were dissolved in chloroform to yield 1% (wt/vol) solutions. The homogeneous solutions were cast in shallow Teflon-coated trays and the solvent was removed as fast as possible in forced air draft. Solid films, not completely dried but easily handlable, were obtained within several seconds. Once dried under vacuum, their thickness ranged usually between 0.3 and 0.6 mm. The samples were then prepared for examination with a transmission electron microscope using a Reichert OMU3-FC2 microtome. They were first embedded in Maraglas (Ladd Research Ind., Inc.) epoxy embedding medium which was hardened by curing at 50 °C overnight. The embedded samples were sectioned at room temperature using water as a receiving medium. Ultrathin sections of 500 to 900 Å in thickness were obtained. The sections were each mounted on a 200-mesh nickel grid. They were examined with a Hitachi HU-11C transmission electron microscope at 75 kV using a low beam current at magnifications of 24 000 and 52 000 times. Several grids were prepared from each sample, and several photographs were taken from each grid. The photographs presented in this paper are true representatives of the corresponding samples.

The unperturbed radius of gyration R_{G0} of the tagged IPS, as calculated[4] from the $M = 2 \times 10^6$ of the parent PS, is 390 Å; in a good

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