Solid-State Structure of Comb-Like Polymers Having *n*-Octadecyl Side Chains I. Cocrystallization of Side Chain with *n*-Octadecanoic Acid

Katsuhiko INOMATA, Yoshiaki SAKAMAKI, Takuhei NOSE, and Shintaro SASAKI*

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

*Department of Chemical Materials Science, School of Materials Science,
Japan Advanced Institute of Science and Technology,
Asahidai, Tatsunokuchi, Ishikawa 923-12, Japan

(Received June 6, 1996)

ABSTRACT: Solid-state structures of comb-like polyacrylates (PAx) and polymethacrylates (PMx) having crystallizable *n*-octadecyl side chains and their blends with *n*-octadecanoic acid (C18) have been investigated by means of differential scanning calorimetry and X-ray diffraction methods. It is concluded that *n*-alkyl side chains of comb-like polymer cocrystallize with low-molecular-weight C18 by incorporation of C18 into hexagonal crystalline lattice. In the case of amorphous PMx, the addition of C18 can induce a formation of crystalline domain by the cocrystallization with the side chain. Differences in the crystallization behavior, such as fractions of crystallized methylene units and effects of thermal history, between PAx and PMx are found to be considerably large. These results are explained by the difference in the segmental mobility of main chain.

KEY WORDS Comb-Like Polymer / *n*-Octadecanoic Acid / Cocrystallization / X-Ray Diffraction / DSC Measurement / *n*-Alkyl Side Chain /

Differences in solid-state nature between side chain and main chain in comb-like polymers are anticipated to give a wide variety of phases, structures, and morphologies, for example, those in side-chain liquid crystalline polymers¹ and rigid-rod polymer with flexible side chains.^{2–4} Comb-like polymers, which have crystallizable long *n*-alkyl side chains being attached to amorphous main chain, are known to pack into layered structure with alternating crystalline side-chain region and amorphous main-chain region in the solid state.^{5–13} Platé and Shibaev⁶ studied these comb-like polymers extensively. X-Ray diffraction profile for such polymer has an intense reflection corresponding to the Bragg spacing *d* of 4.2 Å, which suggests a formation of hexagonal crystalline lattice of *n*-alkyl side chain. There also exists a reflection in smaller angle region, which is considered to originate from the layered structure. The repeating distance of crystalline-amorphous layer can be obtained by the diffraction angle of this reflection. Platé *et al.*⁶ observed striking difference in the diffraction patterns and layer spacings between comb-like polyacrylates and polymethacrylates. In order to interpret this difference, they proposed two models for chain packing: two-layer structure and one-layer structure for respective polymers. In the former model, the side chains are extended on both side of the main chain and these polymers pack closely because of the flexibility of the main chain. In the latter structure, the disordered packing of the end groups of side chains occurs because of the increased bulkiness of the main chain, and the polymer chains are arranged with a shift toward the extended side-chain axis. Later, Hsieh *et al.*⁹ proposed a new structural model for the solid state poly(*n*-octadecyl methacrylate), where the side-chain crystallites are formed by intercalating side chains pointing in opposite directions. Although the detailed solid-state structures of these comb-like polymers have not been clarified as yet, the layered structure with the alternating segregation of side-chain and main-chain layer is commonly

accepted.^{5–13} In this series of studies, we aim to investigate solid state nature of comb-like polymers comprising amorphous main chain and crystallizable side chains.

These polymers are used as pour-point depressants for lubricating oils or fuels. This depressant effect is considered to work by the ability of the polymers to cocrystallize with *n*-paraffins into the same crystalline lattice.^{14–19} Rubin and Pugliese^{15–18} investigated thermodynamical and structural changes of solidified *n*-paraffins containing poly(*n*-alkyl methacrylate)s. In the solid state of poly(*n*-octadecyl methacrylate) blended with *n*-dodecane and *n*-octacosane, side chains of the polymer were found to cocrystallize with *n*-hydrocarbons and to alter the solid-state structure of low-molecular-weight component. From a viewpoint of thermally reversible gel formation, Platé and Shibaev⁶ studied the solution of comb-like polymers in solvent such as *n*-aliphatic hydrocarbons and alcohols. From these findings in literature, it is expected that the similarity of chemical and crystal structure between those of side chain of comb-like polymer and *n*-aliphatic compound will lead their blends to various phases and morphologies in solid state.

In this paper, we focus our attention on cocrystallization behavior of blends of comb-like polymers with *n*-octadecanoic acid (CH₃(CH₂)₁₆COOH, C18). As the comb-like polymers, we adopt polymethacrylates and polyacrylates having *n*-octadecyl residue as the side chain: statistically random copolymer poly[(methyl methacrylate)-*stat*-(*n*-octadecyl methacrylate)] and poly[(methyl acrylate)-*stat*-(*n*-octadecyl acrylate)]. The *n*-alkyl fatty acid C18 has chemical structure similar to that of the side chain of polymers, and crystallizes at a temperature higher than crystallization temperatures of polymers. Influences of main-chain structure, composition of the *n*-octadecyl residue in pure polymers, and blend composition upon the phase behavior are systematically studied. Morphological changes accompanied with

these factors will be reported in detail in Part II of this series.²⁰

EXPERIMENTAL

Materials

Methyl acrylate and methyl methacrylate were treated with aqueous alkali to remove inhibitor, dried, and distilled before use. *n*-Octadecyl acrylate, *n*-octadecyl methacrylate, and *n*-octadecanoic acid (C18) were commercially available and used without purification. Polymerizations and random copolymerizations^{7,9} of the above monomers were carried out in a solution of toluene at 60°C for three days with the use of 0.5 mol% azobisisobutyronitrile as initiator. The reacted mixtures were poured into acetone or hot methanol. The precipitated polymers were washed with acetone or hot methanol till free of monomers. The *n*-octadecyl-side-chain compositions of the copolymers were determined by ¹H NMR spectra. Hereafter, a polymer which contains *x* mol% *n*-octadecyl ester residue is designated as PA*x* for polyacrylates and PM*x* for polymethacrylates. Sample codes and molecular weights of the prepared samples are listed in Table I. In cooling scan of differential scanning calorimetry (DSC) measurement for these polymers from the molten state, a sharp exothermic peak was observed for all the series of polyacrylates and for polymethacrylates of high *n*-octadecyl side-chain composition: PA100, PA70, PA54, PA33, PM100, PM71, and PM53. These polymers also exhibited a sharp X-ray diffraction peak at wide-angle region, which suggests the formation of hexagonally-packed crystallite of the *n*-alkyl side chains. On the other hand, PM43 and PM16 showed no transition peak in DSC thermogram and no crystalline diffraction in X-ray profile.

The blend samples of comb-like polymer with C18 were prepared as follows. The weighted polymer and fatty acid were dissolved in tetrahydrofuran (THF), casted on Teflon sheet, heated at 90°C, quenched to room temperature, and dried in vacuum. Blends of high fatty acid content were ground to fine powder in order to prepare homogeneously-mixed samples. The compositions of the blends are expressed by the mole fraction of the monomeric unit of polymer and C18 molecule.

Methods

DSC thermograms were recorded by using a Perkin-

Elmer DSC model II instrument, and indium was used as the reference for correcting heat of transition. X-Ray diffraction measurements were performed with Ni-filtered Cu-*K*α radiation (wave length $\lambda = 1.5418 \text{ \AA}$) generated from RU-200BH (Rigaku Co.) and an imaging plate detector (R-Axis IID, Rigaku Co.). All measurements were carried out at room temperature. The distance between the sample and the imaging plate was calibrated by the 111 reflection of silicon powder sprinkled over the sample. Diffraction diagram recorded on the flat imaging plate by normal-beam-transmission technique was converted to the one-dimensional profile against diffraction angle 2θ . The Bragg spacing *d* was given by the equation $d = \lambda / (2 \sin \theta)$. Size-exclusion chromatography (SEC) was run on Toyo-Soda HLC 803 using THF as eluent. The columns were calibrated with linear narrow molecular weight polystyrenes.

RESULTS AND DISCUSSION

Cocrystallization of C18 with *n*-Octadecyl Side Chain of PA*x* and PM*x*

Figure 1 shows the composition-dependence of DSC thermograms of the blend system of PA54/C18 measured by cooling with a rate of 20 deg min⁻¹ from melt state. A peak corresponding to side-chain crystallization is observed at 35°C for the pure PA54. There is also one exothermic peak for the blends with less than 16 mol% C18 content. For the samples of higher C18 contents, another exothermic peak is observed at higher-temperature region. With the increase of C18 content, the position of this peak moves toward that of pure C18 (62°C). Similar thermograms are also obtained for the blends of the other side-chain crystallizable polymers (see Experimental) with C18. Exceptionally, the thermograms of PA100/C18 system show some complicated behavior. Details will be described in Part II of this series.²⁰

X-Ray diffraction measurements of the PA54/C18 blend samples cooled rapidly from the melt were carried out at room temperature. Thus prepared samples were confirmed to exhibit nearly identical DSC heating thermogram with that for the sample cooled at the rate of 20 deg min⁻¹ in DSC instrument. Results are shown in Figure 2. In the diagram of pure PA54 (bottom of Figure 2), two intense reflections are observed at diffraction angles $2\theta = 2.7^\circ$ and 21.5° . The former corre-

Figure 1. DSC cooling thermograms for PA54/C18 systems with C18 contents of 0, 16, 24, 43, and 100 mol%, measured at the rate of 20 deg min⁻¹.

Table I. Characteristics of sample polymers

	Code	Fraction of octadecyl ester residue/mol% ^a	<i>M_w</i> ^b
Polyacrylates	PA100	100	190000
	PA70	70	160000
	PA54	54	150000
	PA33	33	140000
Polymethacrylates	PM100	100	440000
	PM71	71	230000
	PM53	53	170000
	PM43	43	120000
	PM16	16	70000

^a Determined by ¹H NMR spectra.

^b Determined by SEC analyses (calibrated by polystyrene).

Figure 2. X-Ray diffraction diagrams for PA54/C18 systems with C18 contents of 0, 16, 24, 43, and 100 mol%, measured at room temperature. The baseline for each diagram is shifted up and down in order to avoid overlapping. The peaks designated by $\times$ correspond to those of silicon sprinkled on the sample.

sponds to the layered structure of the alternating crystalline side-chain region and amorphous region, and the latter to hexagonal packing of *n*-alkyl chain. In the diffraction patterns of blends with 16 mol% C18 content or less, only these two peaks are observed with varying their relative intensities: addition of C18 causes decrease in intensity of the reflection at smaller angle and increase at wider angle. For samples containing more than 24 mol% C18, some additional peaks appear and increase in intensity with C18 content (indicated by the arrow in Figure 2). At the top of Figure 2, the diffraction pattern of pure C18 is presented. It is known that C18 molecule crystallizes into some polymorphs.^{21–24} From the intensity and spacing of each observed reflection, the crystalline form of C18 prepared in this work is considered to be of C-form.²² Comparison of profiles of the pure C18 and blend PA54/C18 containing more than 24 mol% C18 indicates that the newly appeared peaks can be assigned to the crystallite in C-form of C18. From these observations, we may say that there exists only hexagonally-packed crystalline lattice in the sample containing less than 16 mol% C18, which is suggested by the absence of the X-ray diffraction peaks and DSC transition peaks corresponding to pure C18. In the blends containing more than 24 mol% C18, the isolated C18 crystallites are coexisting with the hexagonal crystalline lattice. Similar X-ray diffraction profiles are also observed in the blends comprising another side-chain crystallizable polymer and small amount of C18.

Figure 3 shows DSC thermograms of PM43 and its blends with C18 measured at the cooling rate of 20 deg min⁻¹. Absence of any crystallization peaks in the thermogram of pure PM43 indicates that this comb-like polymer do not form crystalline domain in the solid state. However, its blend of 7 mol% C18 content gives a transition peak at ~10°C, which is nearly the crystallization temperature of pure PM53. In the X-ray

Figure 3. DSC cooling thermograms for PM43/C18 systems with C18 contents of 0, 7, 15, and 100 mol%, measured at the rate of 20 deg min⁻¹.

Figure 4. X-Ray diffraction diagrams of PM43 and PM43/C18 blend with 7 mol% C18 content, measured at room temperature. The baseline for each diagram is shifted up and down in order to avoid overlapping. The peaks designated by $\times$ correspond to those of silicon sprinkled on the sample.

diffraction diagram of pure PM43 (Figure 4), there can be seen amorphous halo around $2\theta = 18^\circ$, and intense but broad peak at smaller angle region which is considered to originate from the correlation between the segregated side chain and main chain. For PM43/C18 blend with 7 mol% C18, there exists a weak shoulder peak at $2\theta = 21^\circ$ (indicated by the arrow in Figure 4) which can be assigned to the hexagonal packing of *n*-alkyl chain. These observations suggest that the addition of C18 induces the crystallization of the side chain for the amorphous comb-like polymers. Similar results are also observed in PA16/C18 system.

For the blends which give a single crystallization peak in the DSC cooling thermogram, we calculate heat of crystallization for one mole of octadecyl side chain, ΔH_{side} . ΔH_{side} will not change with the C18 content if the added C18 does not influence the crystallization behavior of the side chain. These values are plotted against the mole fraction of C18 in Figure 5. The increase of ΔH_{side} with C18 content indicates the increase of the number of methylene unit in the hexagonally-packed crystalline domain. It can be pointed out that the blended C18 molecules are incorporated into the crystalline lattice formed by the side chains of polymer when amount of the added C18 is small, that is to say, C18 molecules are cocrystallizing with *n*-octadecyl side chains in solid state.

Figure 5. Plots of the heat of crystallization per mole of *n*-octadecyl side chain, ΔH_{side} , against the mole fraction of C18 in the blends $\text{PA}_x/\text{C18}$ and $\text{PM}_x/\text{C18}$: (○) PA100, (△) PA70, (□) PA54, (◇) PA33, (●) PM100, (▲) PM71, (■) PM53, and (◆) PM43.

Figure 6. X-Ray diffraction diagrams for PA100 and PA70/C18 systems with C18 contents of 0, 5, 9, and 18 mol%, measured at room temperature. The baseline for each diagram is shifted up and down in order to avoid overlapping.

Figure 6 is the X-ray diffraction diagrams in small-angle region for pure PA100 and blends of PA70/C18. There is a sharp reflection at $2\theta = 2.9^\circ$ ($d = 30 \text{ \AA}$) in the diagram of pure PA70, while PA100 gives a somewhat broad peak at $2\theta = 2.1^\circ$ ($d = 42 \text{ \AA}$). As seen in the figure, the scattering intensity around 2.1° observed in the profile of PA70/C18 blend is gradually increased with the C18 content. For the samples containing C18 to the extent of 18 mol%, no evidence of crystallization of isolated C18 is recognized in DSC thermogram and wide-angle X-ray profile. Thus, the reflection at 2.1° for the blend sample do not suggest the formation of C18 crystallite but the formation of the layered structure observed in PA100. This result means that the cocrystallization of C18 with the side-chain crystalline lattice and the increase of the composition of side chain of comb-like polymer have a similar effect on the packing manner of the chain. Figure 6 also suggests the coexistence of two kinds of layered structures in PA70/C18 blends, one is observed in PA70, and the other in PA100. This observation indicates that the arrangement of the crystalline and amorphous layers varies with the fraction of *n*-alkyl chain in the system. More detailed discussion concerning with the layered structure will be presented

Figure 7. Plots of ΔH_{alkyl} , the heat of crystallization per mole of *n*-alkyl chain including *n*-octadecyl side chain and C18, against the fraction of C18 in all *n*-alkyl chain ($= \text{C18}/(\text{C18} + \text{side chain})$). Symbols are the same as in Figure 5.

in Part II of this series.²⁰

Effect of Main-Chain Structure

In the preceding section, we obtained the heat of crystallization per mole of *n*-octadecyl side chain, ΔH_{side} , for the blend samples. From the increase of ΔH_{side} with C18 content, we have suggested the cocrystallization of the comb-like polymer with C18. In order to consider the state of the crystalline domain containing both *n*-octadecyl side chain and C18, we calculate ΔH_{alkyl} , which is defined as the heat of crystallization for one mole of *n*-alkyl chain: including both *n*-octadecyl side chain and C18 molecule. The values of ΔH_{alkyl} are plotted against the fraction of C18 in the total *n*-alkyl chain ($\text{C18}/(\text{C18} + \text{side chain})$) in Figure 7. As shown in this figure, ΔH_{alkyl} is increased with the increase of C18 content for both PM_x and PA_x series. This result suggests that the cocrystallization behavior of comb-like polymer with C18 increases the averaged number of methylene unit, which existing in the hexagonally-packed crystalline domain, in one *n*-alkyl chain. In the series of PA_x (open symbols in Figure 7), all data points can be expressed by a single line. Extrapolation of this line to 100% of C18 composition gives the value of ΔH_{alkyl} as $11.5 \text{ kcal mol}^{-1}$. Heat of melting for the hexagonal modification of the *n*-alkane has been reported as $0.73 \text{ kcal per mole of methylene unit}$,^{8,25} then heat of transition for sixteen methylenes can be calculated as $11.7 \text{ kcal mol}^{-1}$, which is comparable with the extrapolated value of ΔH_{alkyl} .

In the case of the series of PM_x , ΔH_{alkyl} varies with the change of x as shown by the filled symbols in Figure 7, which is different from the case of PA_x . This tendency has been explained by difference in the mobility of the segmental motion of the main chain.⁸ Melting temperature of the hexagonally-packed *n*-alkyl side chain is $10\text{--}40^\circ\text{C}$, which is higher and lower than the glass transition temperature, T_g , of poly(methyl acrylate) and poly(methyl methacrylate), respectively. Thus, the segmental motion of the main chain of PM_x may be considerably restricted at the crystallization temperature of *n*-alkyl side chain. In the case of PA_x series, the flexibility of the main chain may facilitate the crystallization of the side chains.

In order to examine the effect of the main chain upon

Figure 8. Plots of ΔH_{alkyl} against f_{main} , which is defined as the ratio of the number of repeating unit of the main chain to the number of the n -alkyl chain. Symbols are the same as in Figure 5.

the crystallization behavior of the side chain, we define the ratio of the number of repeating unit of the main chain ($-\text{CH}_2-\text{CH}-$ for PAX and $-\text{CH}_2-\text{C}(\text{CH}_3)-$ for PMx) to the number of n -alkyl chain (both n -octadecyl side chain and C18 molecule) as f_{main} . The value of f_{main} represents a relative amount of main-chain group against the crystallizable n -alkyl chain. As shown in Figure 8, the series of PMx have a linear relation between f_{main} and ΔH_{alkyl} , which is a contrast to PAX series represented by the open symbols. This figure suggests that, for PMx , the crystallization of n -alkyl chain are under strong influence of the existence of the main chain. The extrapolated value of ΔH_{alkyl} to $f_{\text{main}}=0$ is $9.1 \text{ kcal mol}^{-1}$, which is a little smaller than the calculated heat of fusion of sixteen hexagonally-packed CH_2 groups ($11.7 \text{ kcal mol}^{-1}$). From Figures 7 and 8, we can say that the crystallization behavior of n -alkyl chain is nearly independent of the presence of the main chain for PAX , and for PMx , the main chain strongly influences the crystallization behavior of n -alkyl chain.

Effect of Thermal History

In order to investigate the manner of cocrystallization of C18 with the side chain, we have measured DSC heating thermogram of blends which have been undergone different thermal history. In the cooling thermogram of blend of PM100/C18 with 23 mol% C18 content measured at the rate of 20 deg min^{-1} from the melt state, there appears a single exothermic peak which corresponds to the cocrystallization of the side chain with C18. The curve a in Figure 9 is the heating thermogram of this quenched sample, measured at the rate of 10 deg min^{-1} . Just behind a sharp endothermic peak at 41°C , an exothermic peak exists, and after that, second endothermic peak is observed at 63°C . The endothermic peaks at lower and higher temperature are considered as the melting of the hexagonally-cocrystallized domain and the isolated C18 crystallite, respectively. Curve b in Figure 9 is the heating thermogram of the blend with the same composition, which has been first quenched from the molten state, annealed at 54°C (the middle point of the two endothermic peaks) for a few minutes, and subsequently cooled to -13°C with the rate of 5 deg min^{-1} . In b, the exothermic peak between the two endothermic peaks can not be observed, and peak

Figure 9. DSC heating thermograms for PM100/C18 system with 23 mol% C18 measured at the rate of 10 deg min^{-1} . Sample for (a) is rapidly cooled (20 deg min^{-1}) from molten state, and sample for (b) is obtained by annealing the rapidly cooled sample at 54°C .

Figure 10. X-Ray diffraction diagrams measured at room temperature. (a) PM100, (b) PM100/C18 with 23 mol% C18 content crystallized from molten state by the cooling rate of 20 deg min^{-1} , (c) the same composition as (b) but crystallized after annealing at 54°C , and (d) C18. The baseline for each diagram is shifted up and down in order to avoid overlapping. The peaks designated by $\times$ correspond to those of silicon sprinkled on the sample.

area of the endothermic peak at lower temperature is decreased.

The X-ray diffractograms for the samples undergone the identical thermal treatments as mentioned above are shown in Figure 10. All the measurements have been conducted at room temperature. In the diagram of the quenched sample (Figure 10b), there are only two diffraction peaks as that of pure PM100 (Figure 10a), which suggests the occurrence of the cocrystallization. Figure 10c shows the profile of the sample annealed at 54°C . There exist some additional reflections such as at $2\theta=2^\circ$ and 24° , and these can be assigned to the pure C18 crystallite shown in Figure 10d. These variations in the thermogram and X-ray profile depending on the thermal history are also observed for the blends of other side-chain crystallizable PMx , but negligible for the blends of PAX series.

These phenomena give information concerning the manner of the cocrystallization of C18 with the side chain. When the blend of polymethacrylate with C18 is cooled rapidly, the formation of pure C18 crystallite may be considerably prohibited because of the rapid cooling and the restricted segmental motion of the main chain, and the cocrystallization of side chain may occur with excess amount of C18 molecules as compared with the equilibrium condition. Heating of this solid cause

the melting of the cocrystallized domain, and the incorporated excess C18 molecules become free and crystallize by themselves again because the temperature is lower than the melting point of pure C18. The crystallization of C18 gives the exothermic peak in the heating thermogram as seen in Figure 9a. In the subsequent cooling scan from 54°C, the side chains cocrystallize with less amount of C18 because some C18 crystallites have already been formed during the annealing. As a result, the area under the melting peak at lower temperature is decreased and the exothermic peak disappears in the subsequent heating thermogram (Figure 9b). In the case of the series of polyacrylates, the segmental mobility of the main chain is higher than that of polymethacrylates, and the crystallization of C18 may not be severely hindered even in the rapid-cooling process. The difference between the thermogram of rapidly-cooled PM x blend and that of the annealed one suggests the occurrence of the cocrystallization of C18 with the side chains.

CONCLUDING REMARKS

Solid-state structures of the blends of comb-like polymers having n -octadecyl side chains (PA x and PM x) with n -octadecanoic acid (C18) are investigated by means of DSC and X-ray diffraction methods. PM x having more than 43 mol% n -octadecyl ester residue and all PA x are crystalline polymers, in which side chains form hexagonally-packed crystalline lattice. The side chains of these polymers are cocrystallizing with C18 by incorporation of C18 into the crystalline lattice of the side chain. Although the pure PM43 and PM16 can not form crystalline domain, the addition of C18 to these polymers induces the formation of hexagonal crystallite by the cocrystallization of C18 with the side chain. The cocrystallization phenomenon increases the number of methylene unit which existing in the crystalline domain, and changes the crystalline-amorphous layered structure as seen in PA70/C18 system. The difference in the crystallization behavior, *i.e.*, the C18-content dependence on ΔH_{alkyl} or the effect of thermal history, between PA x and PM x is large, probably because of the difference in the segmental mobility of the main chain. These systematic studies indicate a possibility to control the solid-state nature of the side-chain crys-

tallizable comb-like polymers and their blends with n -alkyl chain. In Part II of this series,²⁰ we will report a possibility of the control of the layered structure in solid state for these systems.

REFERENCES

1. V. P. Shibaev and N. A. Platé, *Adv. Polym. Sci.*, **60/61**, 173 (1984); V. P. Shibaev, Ya. S. Freidzon, and S. G. Kostromin, in "Liquid Crystalline and Mesomorphic Polymers," V. P. Shibaev and L. Lam, Ed., Springer-Verlag, New York N.Y., 1994, p. 77.
2. M. Ballauff, *Angew. Chem. Int. Ed. Eng.*, **28**, 253 (1989).
3. J. Watanabe, H. Ono, I. Uematsu, and A. Abe, *Macromolecules*, **18**, 2141 (1985).
4. J. Watanabe, B. R. Harkness, M. Sone, and H. Ichimura, *Macromolecules*, **27**, 507 (1994).
5. S. A. Greenberg and T. Alfrey, *J. Am. Chem. Soc.*, **76**, 6280 (1954).
6. N. A. Platé and V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, **8**, 117 (1974).
7. E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci., A-1*, **9**, 1835 (1971).
8. E. F. Jordan, Jr., B. Artymyshyn, A. Specca, and A. N. Wrigley, *J. Polym. Sci., A-1*, **9**, 3349 (1971).
9. H. W. S. Hsieh, B. Post, and H. Morawetz, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1241 (1976).
10. J. M. Barrales-Rienda, F. Fernandez-Martin, C. R. Galicia, and M. S. Chaves, *Makromol. Chem.*, **184**, 2643 (1983).
11. K. Yokota, T. Kougo, and T. Hirabayashi, *Polym. J.*, **15**, 891 (1983); K. Yokota and T. Hirabayashi, *Polym. J.*, **18**, 177 (1986); T. Hirabayashi and K. Yokota, *Polym. J.*, **19**, 1115 (1987).
12. L. J. Mathias, *Polym. Commun.*, **29**, 352 (1988).
13. P. L. Magagnini, E. L. Tassi, F. Andruzzi, and M. Paci, *Polym. Sci.*, **36**, 1502 (1994).
14. E. F. Jordan, Jr., S. Smith, Jr., R. D. Zabarsky, and A. N. Wrigley, *J. Appl. Polym. Sci.*, **22**, 1509 (1978); 1529 (1978); 1547 (1978).
15. I. D. Rubin, *J. Appl. Polym. Sci.*, **36**, 445 (1988).
16. I. D. Rubin and R. D. Pugliese, *Angew. Makromol. Chem.*, **171**, 165 (1989).
17. R. D. Pugliese and I. D. Rubin, *Macromol. Rep.*, **A28**(Suppl. 2), 111 (1991).
18. R. D. Pugliese and I. D. Rubin, *Polym., Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **33**, 340 (1992).
19. A. K. Chatterjee, S. D. Phatak, P. S. Murthy, and G. C. Joshi, *J. Appl. Polym. Sci.*, **52**, 887 (1994).
20. K. Inomata, S. Sakamaki, T. Nose, and S. Sasaki, *Polym. J.*, **28**, 992 (1996).
21. K. Larsson and E. Sydow, *Acta Chem. Scand.*, **20**, 1203 (1966).
22. V. Malta, G. Celotti, R. Zannetti, and A. F. Martelli, *J. Chem. Soc. (B)*, 548 (1971).
23. M. Goto and E. Asada, *Bull. Chem. Soc. Jpn.*, **51**, 2456 (1978).
24. M. Gotoh, *J. Jpn. Oil Chem. Soc.*, **36**, 909 (1987).
25. M. G. Broadhurst, *J. Res. Nat. Bur. Stand.*, **66A**, 241 (1962).