Thermal Analysis and NMR Observation of 66-Nylon

Masayoshi Ito, Tetsuo Kanamoto, and Koji Tanaka

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received October 1, 1976)

The effects of morphology on γ-relaxation in 66-Nylon is investigated. The morphology of the samples was characterized mainly by thermal analysis. Information about the molecular motion of 66-Nylon is obtained from the temperature dependence of the spin-lattice relaxation times (T_1). In order to compare the relaxation behavior of 66-Nylon with that of other semicrystalline polymers, the T_1 of polyoxymethylene (POM) was also measured as a function of temperature. It was found that in 66-Nylon, both solution-grown crystals and bulk samples are composed of folded chain lamellae with fairly large amounts of less perfect crystalline regions. Both the magnitude and the temperature of the T_1 minimum at about 30 °C (γ-region) for 66-Nylon are not sensitive to the sample history, in contrast to those for POM. In addition, the T_1-temperature curve in the γ-region for 66-Nylon is much broader than that for POM. These NMR results for 66-Nylon are interpreted in terms of a rather wide variety of structural heterogeneities from the usual amorphous regions to fairly restricted regions, such as the less-perfect crystalline regions at the lamellar surface.

It is well known that 66-Nylon has three principal relaxations α, β, and γ, in the decreasing order of the temperatures at which they occur.[1] The α-relaxation corresponds to the glass transition[1] and the β-relaxation is related to the motions of polar groups.[2] For the γ-relaxation, different results and explanations have been presented,[3-5] and a complete understanding of this relaxation is still lacking. Bell and Murayama[3] have reported that for 66-Nylon, melt-quenched sample exhibits mechanical γ-dispersion, while slowly-cooled and cold-drawn samples do not show this dispersion. These samples can be characterized from their melting behavior: the former has folded chain crystals and the latter two have less-perfect bundle crystals.[6] Olf and Peterlin[4] have proposed, on the basis of NMR data of drawn fibers of 66-Nylon, that the origin of the γ-relaxation is related to the motions of strained tie molecules. These suggest that 66-Nylon exhibits complex γ-relaxation related to various morphological origins. Hence, the morphological characterization of the sample is very important for understanding the γ-relaxation of 66-Nylon. In this study, thermal analysis, infrared spectroscopy, and density measurements were employed to make a detailed characterization of the morphology of the samples.

Information about the molecular motion of 66-Nylon for a variety of morphologies is obtained from the temperature dependence of the spin-lattice relaxation times (T_1). The relaxation behavior of 66-Nylon is compared with that of polyoxymethylene for which the relaxation mechanisms are well defined.[7,8] Marked differences between them are observed for γ-relaxation and are discussed in light of a morphological interpretation of 66-Nylon.

Experimental

Samples. Commercial 66-Nylon (Toray Co., Ltd.) was dissolved in formic acid and precipitated in an excess of methanol in order to remove impurities. After repeated washing with methanol, the polymer was dried *in vacuo* at 100 °C for one week. Morphological varieties of the samples were prepared by the following procedures.

Solution-crystallized 66-Nylon: *(1) Rapidly-cooled solution grown (SGQ) sample*: One gram of 66-Nylon was dissolved in one liter of glycerin at 220 °C for 40 min, and then the solution was cooled to room temperature at a rate of 30 °C/h. The precipitated crystals were washed with methanol several times and then dried *in vacuo* at 80 °C for one week. *(2) Isothermal solution grown (SGI) sample*: 0.5 g of 66-Nylon was dissolved in one liter of 1,4-butanediol at 180 °C for 15 min, and then the crystals were precipitated at 114 °C for 42 h. The washing and drying procedures for the crystals were identical with those for the SGQ sample.

Observation by electron microscopy indicated that these crystals consist of multilayer single crystals and two dimensional open spherulites.

Bulk-crystallized 66-Nylon: Various bulk-crystallized 66-Nylon specimens were prepared by the treatment similar to those described by Bell and Dumbleton.[6] The polymer samples, sealed in glass tube *in vacuo*, were heat-treated, melt-quenched (MQ) sample, annealed after melt quenching (MQA) sample, slowly-cooled (SC) sample, and annealed after slow cooling (SCA) sample. The thermal history of the bulk crystallized samples is summarized in Fig. 1.

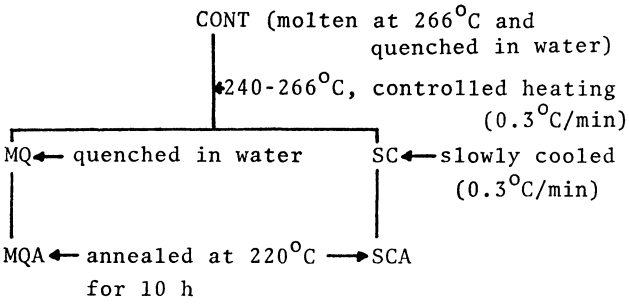

Fig. 1. Shematic representation of the procedures for heat treatment.

Solvent-cast films held in polytetrafluoroethylene sheets and powdered 66-Nylon were heat treated. The melting behavior and densities of the solvent-cast films were substantially identical to those powder samples in regard to the effects of thermal history.

Drawn 66-Nylon Fibers: Drawn fibers were prepared by stretching melt-spun fibers having no orientation to an elongation of about 400% at room temperature.

Polyoxymethylene: Delrin 500 (Du. Pont Co.) was crystallized at several crystallization temperatures. Another sample consisted of extended chain crystals obtained by solid-state

polymerization of trioxane, which was kindly supplied by the Japan Atomic Energy Research Institute, at Takasaki.

Measurements. The melting behavior was observed using a Perkin-Elmer differential scanning calorimeter (DSC-1B), in a nitrogen atmosphere. Sample weights of the order of 1—7 mg were required. The temperature and heat of fusion were calibrated against lead. The melting peak temperature was reproducible for the same sample to within ±0.5 °C.

Pulsed NMR experiments were carried out with a JEOL pulsed NMR (JSE-5) spectrometer, operating at a frequency of 60 MHz. The dead time was 10—12 μs following a 2-μs pulse. 90-τ-90° pulse sequences were used to obtain the proton spin-lattice relaxation times (T_1) to within a precision of ±6% or better. Samples were packed in a sample tube *in vacuo*. Fibers were placed randomly in the sample tube. The sample temperature was regulated to ±0.5 °C by a gas-flow thermostat.

IR spectra were recorded on a JASCO infrared photometer (DS-403G) at room temperature. Spectra of the bulk samples were obtained on films and those of the solution-grown crystals were obtained using samples of about 2 mg in KBr disks.

Densities were determined using a density gradient column at 30 °C in carbon tetrachloride and toluene for 66-Nylon, and in xylene and tetrachloroethylene for polyoxymethlene. The amorphous fraction was calculated using a two-phase model with a crystal density.[9] $\rho_c = 1.24$ g/cm³, and an amorphous density,[9] $\rho_a = 1.09$ g/cm³, for 66-Nylon, and ρ_c[10] = 1.492 g/cm³, ρ_a[11] = 1.25 g/cm³ for polyoxymethylene.

Results and Discussion

Regular Fold Content. Koenig *et al.*[12] have reported that infrared spectroscopy (IR) is a useful method for estimating the regular fold content of 66-Nylon. The regular fold content indexes (the ratio of the absorbances at 1329 and at 936 cm^{-1}) calculated using their method are given in Table 1. All the samples, except the drawn fibers clearly show the regular fold band at 1329 cm^{-1}. It should be noted that the regular fold content indexes for SC and SCA samples, which were previously assumed to be due to a bundle-like crystal structure,[6] have values similar to that for solution-grown crystals (SGI).

Table 1. Characterization data of the samples

Sample	Fold content 1329/936 (IR)	Density g/cm³	Amorphous fraction from density
MQ	0.053	1.162	0.491
MQA	0.059	1.164	0.474
SC	0.074	1.167	0.452
SCA	0.077	1.169	0.440
SGI	0.079	1.190	0.305
SGQ	0.088	1.198	0.250

Thermal Analysis. DSC thermograms for the solution-grown crystals and the heat-treated samples obtained for a heating rate 16 °C/min, are shown in Fig. 2. The MQ and SC samples exhibited a single endothermic peak. On annealing the MQ and SC samples at 220 °C, the former (MQA) produced a new additional peak at a low-temperature side of the original peak, while the latter (SCA) showed no such peak. In solution-grown crystals, the isothermally crystallized SGI sample had double melting peaks, while, the rapidly-cooled SGQ sample gave a single peak.

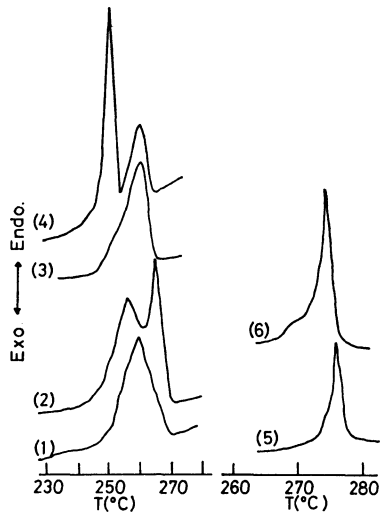

Fig. 2. DSC thermograms of the samples; (1) SGQ, (2) SGI, (3) MQ, (4) MQA, (5) SC, (6) SCA; heating rate was 16 °C/min.

The effect of the heating rate on the melting peaks for the samples are shown in Table 2. When the heating rate was increased, the melting temperature of the SC, SCA, and SGQ samples increased, while that of the MQ and the high-temperature side of the MQA and SGI samples tended to decrease. Such melting behavior of the heat-treated samples agrees well with that of samples used in the dynamic mechanical study by Bell and Murayama.[3]

Table 2. Effect of heating rate on the apparent melting temperature

Heating rate °C/min	Melting temperature, °C							
	MQ	MQA		SC	SCA	SGI		SGQ
2				274	272			
4	263	250	262			255	266	262
8	260	250	261	274	274	256	266	261
16	260	251	260	276	275	257	265	262
32	260			278				266

It has been suggested that extended chain crystals tend to superheat, whereas folded chain crystals do not.[13]

In addition to reorganization during the DSC scan, the thermal diffusivity or temperature gradient in the sample may sometimes affect the melting-peak temperature observed for rapid heating. Indeed, it was found in the present study that even the melting temperature of thin solution-grown crystals (SGQ) (*ca.* 60 Å thick) with typical chain foldings increased with increased heating rate. Furthermore, the samples (SC, SCA) which exhibited apparent superheating showed regular fold bands in their IR spectra. Hence, it was not possible to distinguish between folded chain crystals and extended chain crystals only on the basis of heating-rate dependence of the apparent melting temperature determined by DSC.

In order to reveal the melting behavior inherent in the morphology of the samples, the solution-grown crystals and heat-treated samples were methoxymethylated following the method proposed by Cairns *et al.*[14] This chemical treatment has been found by Arakawa *et al.*[15] to suppress the reorganization of Nylon-6 during thermal analysis, although this has not been applied to 66-Nylon of various morphologies.

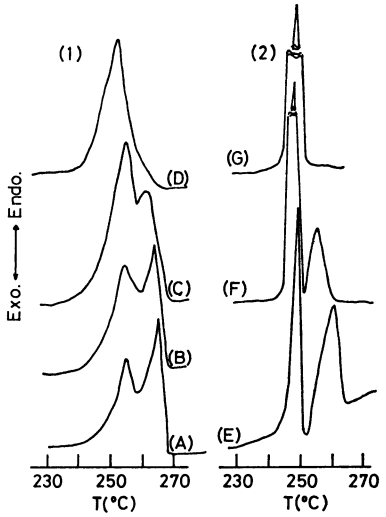

Fig. 3. Changes of melting behavior with methoxymethylation time for (1) MQA, (2) SGI; reaction time was (A) 0 h, (B) 0.7 h, (C) 2 h, (D) 3 h, (E) 0 h, (F) 4 h, (G) 6 h, heating rate was 8 °C/min.

Figure 3 shows the effects of the methoxymethylation time on the thermograms of the MQA and SGI samples obtained for a heating rate of 8 °C/min. The area under the higher melting peak decreased in both samples with increasing reaction time. In the SGI sample, a single melting peak was obtained after a reaction period of 3 h, while the MQA sample exhibited a sharp single peak after 6 h of treatment.

These facts clearly show that the double melting of untreated samples is not associated with the two different lamellar structures, as has been previously deduced from the heating-rate dependence of the melting temperature,[6] but is related to reorganization during the DSC scan

The reaction-time dependence of the melting temperature and the heat of fusion for the solution-grown crystals (SGI) and bulk samples (MQ and SC) are shown in Fig. 4. In all the samples, both the melting temperature and the heat of fusion decreased with increasing reaction time and approached nearly constant values for prolonged reaction times. Such changes were most prominent in the MQ sample. The reduction of the heat of fusion for the MQ, SC, and SGI samples was about 27, 13, and 6%, respectively. The fact that, with the chemical treatment, the heat of fusion decreased initially and reached a nearly constant value for prolonged reaction times indicates that some of the less-perfect crystalline regions or small crystallites were destroyed as a consequence of this treatment. Hence, the observed reduction in the heat of fusion is directly related to the amount of less-perfect crystalline regions

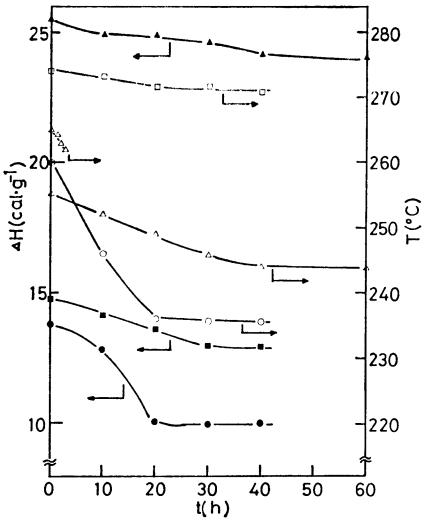

Fig. 4. Changes in the melting temperature with methoxymethylation time for △ SGI, □ SC, ○ MQ; heating rate was 8 °C/min, and changes in the heat of fusion with methoxymethylation time for ▲ SGI, ■ SC, ● MQ.

accessible to the chemical reaction. Although the lowering of the melting points in these samples might be caused primarily by the suppression of the reorganization during the DSC scan, the large decrease in the heat of fusion for the MQ sample suggests that the melting point was also affected by the partial breakdown of the less-perfect regions in the crystallites. In summary, for 66-Nylon, the heat-treated and solution-grown samples were composed of folded chain crystals with different amounts of fold content and of less-perfect crystalline regions depending on the sample history.

NMR Data. The temperature dependence of the spin-lattice relaxation times (T_1) of protons for samples with various morphologies are shown in Figs. 5 and 6. A broad T_1 minimum is present around 30 °C in all the samples studied. In addition to this minimum, the MQ, SC, and SGQ samples showed a small T_1 minimum at 70—80 °C. According to the relaxation map of 66-Nylon,[1,16] the T_1 minima observed here at about 30 and 80 °C at 60 MHz, correspond to the γ- and β-relaxations, respectively, which are usually observed at

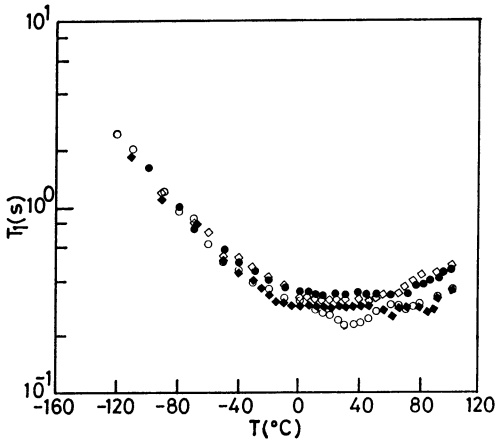

Fig. 5. Temperature dependence of T_1 for ○MQ, ●MQA, ◆SC, ◇SCA.

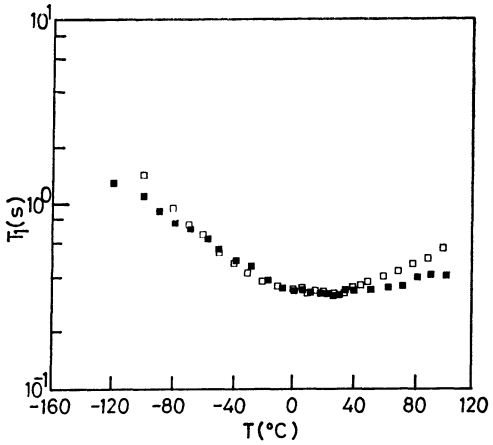

Fig. 6. Temperature dependence of T_1 for ■SGQ, □Drawn Fibers.

around −120 and −40 °C for low-frequency measurement. β-relaxation was found in the MQ, SC, and SGQ samples, but this is not discussed in detail in the present paper.

It should be noted that γ-relaxation in 66-Nylon was found for the SC, SCA, and drawn fibers samples for which other authors[3] failed to detect any mechanical γ-dispersion.

Although the SC, SCA, and drawn fibers samples have been previously considered to be composed of less-perfect bundle crystals,[6] it was confirmed in these measurements using IR and thermal analysis that the SC and SCA samples are composed of the usual folded chain crystals having different amounts of fold content. Furthermore, a large difference in morphology such as in the fold content, might be expected between drawn fibers and solution-grown crystals, these samples have similar spectra for molecular motion in the γ-region. Hence, it is not possible to explain the γ-relaxation in 66-Nylon in terms of only the molecular motions of folded chains at the lamellar surface, as proposed by Bell and Murayama.[3]

In the limit of rapid spin diffusion to the reorienting segments, if the simple two-phase (crystalline-amorphous) model is applicable, the observed maximum relaxation rate $(1/T_1)_{max}$ at the minimum is given by[17]

$$(1/T_1)_{max} = (1-X)/T_1^a, \quad (1)$$

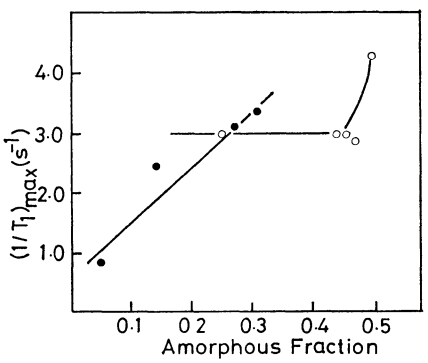

Fig. 7. Maximum relaxation rate at γ-relaxation as a function of the amorphous fraction for ○66-Nylon, ●POM.

where $(1-X)$ is the amorphous fraction and T_1^a is the relaxation time appropriate for the amorphous regions. In Fig. 7, the maximum relaxation rates for the γ-relaxation of 66-Nylon and polyoxymethylene (POM) are plotted against the amorphous fraction calculated from the density. The maximum relaxation rates for POM increased linearly with increasing amorphous fraction. A similar observation for polyethylene and POM has also been reported by Crist and Peterlin.[7,17] For 66-Nylon, on the other hand, all the samples except the MQ sample, exhibited similar relaxation rates despite the fairly large differences in the amorphous fraction.

It is well known that spin diffusion is sufficiently rapid in these γ-regions compared to the dipole-dipole relaxation rate. Therefore, the effects of the amorphous fraction on the maximum relaxation rates for 66-Nylon cannot be explained on the basis of Eq. 1. This means that the simple two-phase model cannot explain the γ-relaxation in 66-Nylon. This is unique to 66-Nylon in comparison with other well-known semicrystalline polymers such as POM[7] and PE,[17] and appears to be important to the understanding of the γ-relaxation in 66-Nylon.

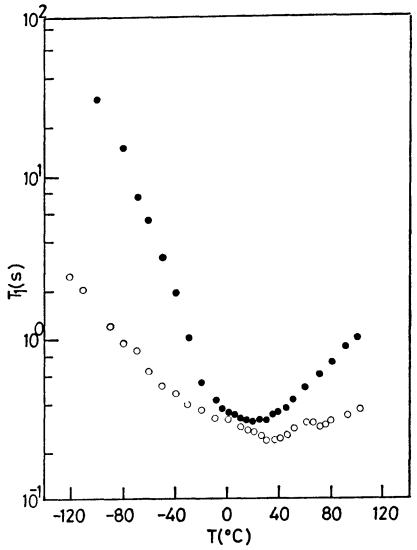

Fig. 8. Temperature dependence of T_1 for ○66-Nylon melt-quenched sample, ●POM melt-quenched sample.

In order to elucidate the characteristic relaxation behavior of 66-Nylon, the temperature dependence of T_1 for 66-Nylon was compared with that for POM for which the γ-relaxation has been explained on the basis of the simple two-phase model[7] in Fig. 8. It is clearly seen that the T_1-temperature curve in the γ-region for 66-Nylon is much broader than that for POM. The broadening of this curve in the higher temperature region could be caused by a coupling of the γ- and β-relaxations. However, this phenomenon in the lower temperature region cannot be caused by coupling with any other relaxation mechanism, because 66-Nylon is known to exhibit no noticeable relaxation below the γ-relaxation.[18] Thus, the broadening indicates that the local mode motions in 66-Nylon have a much wider distribution of correlation times.

Although no fundamental difference (chain folded or extended chain crystals) in the crystalline morphology was found in these bulk samples, they contained, depending on the sample history, different amounts of disordered crystalline regions which were accessible to the chemical reaction.

Atkins *et al.*[19] have carried out an X-ray diffraction analysis of the lamellar structure of 66-Nylon single crystals and found that sharp chain foldings occur at the lamellar surface but that half the lamellar thickness is composed of a less-perfect crystalline core; the chain packing becomes gradually looser in going from the lamellar interior to the fold surface. This type of crystalline disorder in 66-Nylon, which is not found in polyethylene and POM, is considered to occur as the result of a fairly long chemical repetition unit and the small number of such units contained within the lamellar thickness. The observed density defficiency of the SGI sample may be consistent with the lamellar structure revealed by the X-ray diffraction analysis. Hence, the small reduction in the heat of fusion of the solution-grown crystals (SGI) found as a consequence of the chemical treatment indicates that the fraction of the disordered crystalline regions accessible to the chemical reaction was very small. As the bulk samples are thought to be complex aggregates of amorphous materials and crystalline lamellae, it is postulated that both bulk samples and solution-grown crystals contain disordered crystalline regions varying in the degree of perfection from those accessible to the chemical reaction to those revealed by X-ray diffraction.

On considering the above discussions concerning morphology, the structure of the disordered regions of 66-Nylon appears to be very complex compared with those of POM which has a rather short chemical repetition unit and these disordered regions in 66-Nylon appear to consist of a rather wide variety of structural heterogeneity varying from the usual amorphous regions between lamellae or spherulites to fairly restricted regions including those of less-perfect crystalline regions at the lamellar surface. Therefore, it is postulated that the molecular motions in these disordered regions exhibit a wider distribution of correlation times corresponding to the degree of restriction.

Thus, the T_1-temperature curve in the γ-region for 66-Nylon becomes much broader than that for POM.

In summary, γ-relaxation in 66-Nylon cannot be explained by only the motions of the folds or in terms of the simple two-phase model. This relaxation appears to be associated with the motions of segments in the disordered region, which are much more complex than those of POM.

The difference between the dynamic mechanical results previously reported[3] and the present NMR results might be due to the different type and degree of perturbation imposed upon the samples during the measurements. In the NMR experiment, perturbation of the sample system is negligible, but in the dynamic mechanical test, the sample is subjected to a stress and the overall strain on the sample in a complex composition of deformation of the crystalline core and the disordered regions. Indeed, the magnitude of mechanical dispersion has been interpreted in relation to the fine structure of the crystalline polymers using series and parallel models of crystalline and amorphous regions.[20]

The authors wish to express their thanks to Professor Masatami Takeda for continuing interest and encouragement during this investigation.

References

1) N. G. McCrum, B. E. Read, and G. W. Williams, "Anelestic Dielectric Effects in Polymeric Solids," Wiley, London (1967), p. 478.
2) K. H. Illers and H. Jacobs, *Makromol. Chem.*, **39**, 234 (1960).
3) J. P. Bell and T. Murayama, *J. Polym. Sci., A-2*, **7**, 1059 (1969).
4) H. G. Olf and A. Peterlin, *J. Polym. Sci., A-2*, **9**, 1449 (1971).
5) K. H. Illers, *Colloid Polym. Sci.*, **253**, 329 (1975).
6) J. P. Bell and J. H. Dumbleton, *J. Polym. Sci., A-2*, **7**, 1033 (1969).
7) B. Crist and A. Peterlin, *J. Polym. Sci., A-2*, **9**, 557 (1971).
8) A. Tanaka, S. Uemura, and Y. Ishida, *J. Polym. Sci., A-2*, **8**, 1585 (1970).
9) J. B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954).
10) G. Carazzolo, *J. Polym. Sci., A*, **1**, 1573 (1963).
11) C. F. Hammer, T. A. Koch, and J. F. Whitney, *J. Appl. Polym. Sci.*, **1**, 169 (1959).
12) J. L. Koenig and M. C. Agboatwalla, *J. Macromol. Sci., (B)*, **2**, 391 (1968).
13) E. Hellmuth and B. Wunderlich, *J. Appl. Phys.*, **36**, 3039 (1965).
14) T. L. Cairns, H. D. Foster, A. W. Larchar, A. K. Schneider, and R. S. Schreider, *J. Am. Chem. Soc.*, **71**, 651 (1949).
15) T. Arakawa, F. Nagatoshi, and N. Arai, *J. Polym. Sci., A-2*, **7**, 1461 (1969).
16) D. W. McCall and E. W. Anderson, *Polymer.* **4**, 93 (1963).
17) B. Crist and A. Peterlin, *J. Polym. Sci., A-2*, **7**, 1165 (1969).
18) J. M. Crissman, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci., A*, **2**, 5075 (1964).
19) E. D. T. Atkins, A. Keller, D. M. Sadler, and H. H. Wills, *J. Polym. Sci., A-2*, **10**, 863 (1972).
20) M. Takayanagi, M. Yoshino, and K. Hoashi, *Zairyo Shiken*, **10**, 418 (1961).