

Copolyamide의 합성-구조-성질에 관한 연구 IV : 연신된 Copolyamide필름의 열 기계적 성질

조 원 호 · 김 재 호 · 백 두 현

서울대학교 공과대학 섬유공학과
(1986년 8월 12일 접수)

Synthesis-Structure-Property of Copolyamides. IV : Thermomechanical Properties of Drawn Copolyamide Film

Won Ho Jo, Jae Ho Kim, and Doo Hyun Baik

Department of Textile Engineering, Seoul National University, Seoul 151, Korea

(Received August 12, 1986)

Abstract : Caprolactam was copolymerized with hexamethylenediammonium adipate (6,6) and *p*-xylylenediammonium adipate(PXD.6) to form two series of random copolyamides : copolyamide 6/6,6 and copolyamide 6/PXD.6. The thermal shrinkage behaviors of drawn films of copolyamides 6/6,6 and 6/PXD.6 were examined by thermomechanical analyzer(TMA). The shrinkage behaviors of the copolyamides show two characteristic steps with temperature, which can be explained in terms of structural variations. The effects of structure and contents of comonomer units on thermal shrinkage behavior are explained in terms of amorphous and crystalline state.

INTRODUCTION

The thermal shrinkage of oriented polymer is a phenomenon of great importance in determining the end-use potential of a given polymer, and which reflects the process history or the structural state of the polymer. The studies of thermal shrinkage phenomenon can largely be divided into two fields, i.e., one is for the elucidation of the polymer morphology and the other is for the mathematical analysis of the viscoelastic properties of polymers.^{1,2} The thermal shrinkage force under constant length conditions can also be considered for the same objects.³⁻⁵

Although many studies on the thermal shrinkage of polyamide⁶⁻⁸ and PET⁹⁻¹⁴ have been investigated by thermal shrinkage tester combined

with small angle x-ray scattering and infrared spectroscopy, a thorough study on thermal shrinkage of copolyamide is lacking. In the present study, two kinds of copolyamides, poly(ϵ -caprolactam-co-hexamethylenediammonium adipate) (copolyamide 6/6,6) and poly(ϵ -caprolactam-co-*p*-xylylenediammonium adipate) (copolyamide 6/PXD.6) were synthesized and their thermal shrinkage behaviors were analyzed in terms of the structural state in order to elucidate the effects of chemical structure and contents of comonomer units on the structure and properties of the copolyamides.

EXPERIMENTAL

Copolymerization and Copolymer Composition

Determination : Poly(ϵ -caprolactam-*co*-hexamethylenediammonium adipate) and poly(ϵ -caprolactam-*co*-*p*-xylylenediammonium adipate) were synthesized by the method previously reported.¹⁵ The copolymer compositions of copolyamides 6/6,6 and 6/PXD,6 were determined by pyrolysis gas chromatography and ¹H nuclear magnetic resonance spectroscopy, respectively.

Film Preparation : The polyamides were melted between aluminum sheets under pressure in hot press and then quenched in dry ice-acetone bath. Aluminum sheets were eliminated in NaOH solution to obtain amorphous copolyamide films of 70–100 μ m thickness. The films were drawn with draw ratios of 3.0, 3.5, 4.0 and 4.5 in 40°C water bath and the drawn films were cut into fiber form.

Thermal Analysis : A DuPont 943 Thermomechanical Analyzer(TMA) combined with 1090 Thermal Analyzer was used to measure the thermal shrinkage of the drawn samples. The cut film was held between two cleaved aluminum balls 9–10 mm apart, and placed between the hooks of the sample holder and the fiber tension probe, made of quartz. The upper end of the movable fiber probe is connected to a spring which supports the weight of the probe, and makes the initial load of sample zero. Shrinkage was detected by the displacement of the fiber tension probe with LVDT core.

Table 1. The Properties of the Two Copolyamides

Copolymer code	mole% (6,6 or PXD,6)	$[\eta]$, dl/g	T_g , °C	T_m , °C
6, 6,6 4.4	4.4	0.72	43	213
6, 6,6 8.2	8.2	0.95	40	207
6, 6,6 17.5	17.5	0.98	39	189
6, 6,6 26.7	26.7	0.92	40	182
6, 6,6 33.3	33.3	0.98	42	176
6, PXD,6 2.0	2.0	0.82	46	209
6, PXD,6 4.1	4.1	0.51	48	200
6, PXD,6 7.6	7.6	0.90	49	184
6, PXD,6 13.5	13.5	0.72	52	174

The temperature of the sample was raised with a rate of 5°C/min by means of heater assembly placed around the sample and sample holder. Nitrogen was used as a purge gas which prevented reaction of the sample with oxygen and maintained the humidity of the sample at a constant low level. shrinkages were tested more than three times for one sample and the data were taken as an average.

RESULTS AND DISCUSSION

The properties of the copolyamides are listed in Table 1. The glass transition temperature(T_g) of copolyamide 6/6,6 has no significant dependence on copolymer composition since polyamide 6 and polyamide 6,6 have very similar T_g . But, in the case of copolyamide 6/PXD,6, T_g increases with PXD,6 content since the inclusion of aromatic unit into the main chain reduces the chain mobility, thus T_g increases. The melting temperature depression with increasing comonomer content indicates that these two copolyamides are random copolymers.

Fig.2 shows a typical shrinkage thermogram of the copolyamides when heated with a rate of 5°C/min in TMA. The slope of the curve varies with temperature so that the TMA shrinkage thermogram can be divided into several regions with temperature. Each region is named as in the Fig.1. Shrinkages were calculated according to the formula : $S = (\text{dimensional change}/\text{initial})$

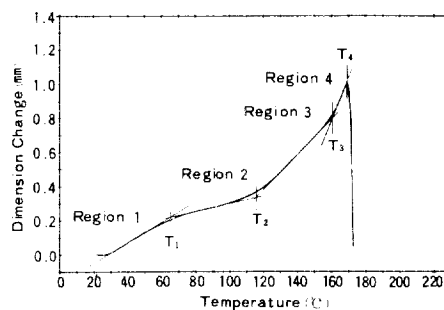


Fig.1. Typical shrinkage thermogram of drawn copolyamide film.

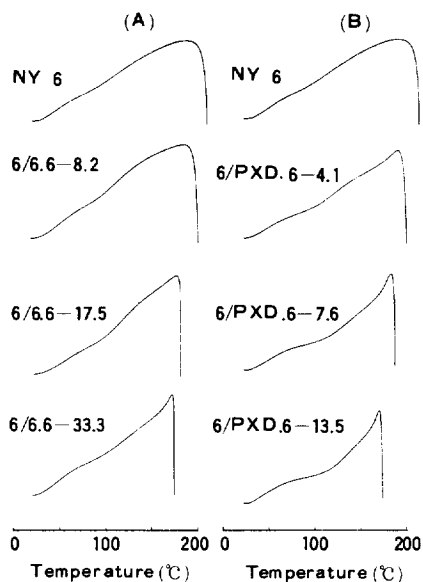


Fig. 2. The shrinkage thermograms of copolyamides 6/6.6(A) and 6/PXD.6(B) with different composition for the draw ratio of 3.0.

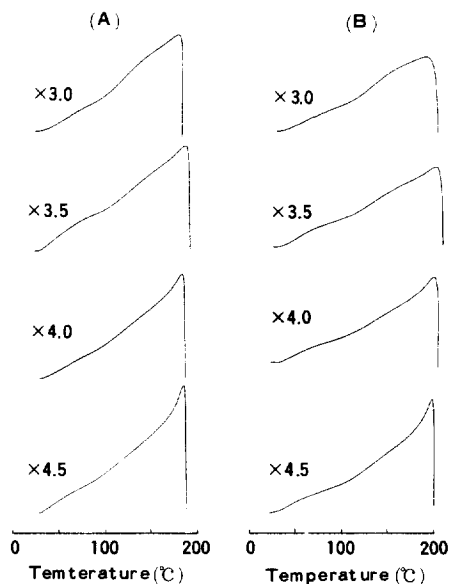


Fig. 3. The shrinkage thermograms of 6/6.6-17.5 (A) and 6/PXD.6-4.1(B) with different draw ratio.

length) $\times 100$. The first derivative of shrinkage, dS/dT , is defined as thermal shrinkage coefficient.

Fig.2 shows the shrinkage thermograms of the

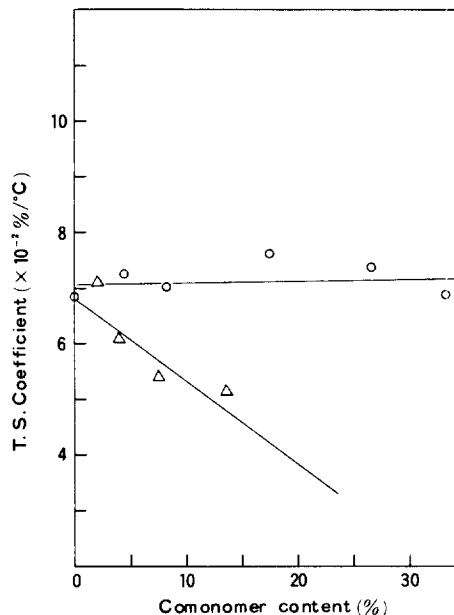


Fig. 4. Effect of comonomer content on the thermal shrinkage coefficient of Region 1 for the draw ratio of 3.0: (○)copolyamide 6/6.6: (△)copolyamide 6/PXD.6.

copolyamides of different composition for draw ratio 3.0. The shrinkage thermograms of copolyamide 6/6.6-17.5 and 6/PXD.6-4.1 with different draw ratios are shown in Fig.3. In general the temperatures of inflection points, thermal shrinkage coefficients and maximum shrinkage coefficients and maximum shrinkage increase as the draw ratio increases. In this study, experiments were carried out for several draw ratios but the results for each draw ratio have the same trends with the comonomer content. Therefore, the data for draw ratio 3.0 are examined mainly and others are used as supplementary data.

Region 1, the shrinkage at low temperature range above T_g , is due to the relaxation of oriented amorphous chains not bound to crystalline region. In this range the relaxation of amorphous region comes from the $-CH_2-$ chain mobility. The hydrogen bond force decreases as temperature increases, but the decrease is not so significant in this temperature range.¹⁶ Fig.4 shows the effect of comonomer content on the thermal

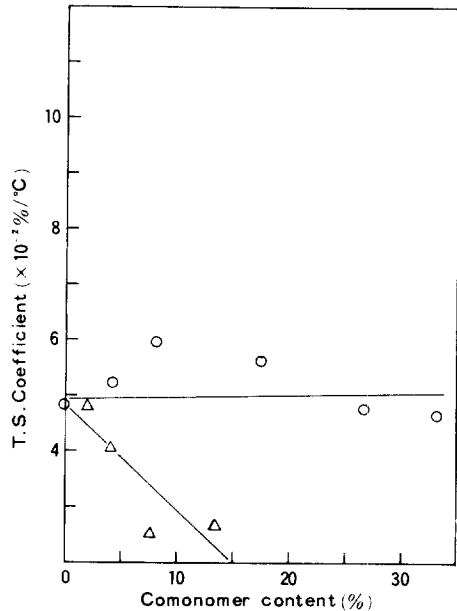


Fig. 5. Effect of comonomer content on the thermal shrinkage coefficient of Region 2 for the draw ratio of 3.0: (○)copolyamide 6/6.6; (△)copolyamide 6/PXD.

shrinkage coefficients of Region 1. The thermal shrinkage coefficient of copolyamide 6/6.6 has no significant dependence on comonomer content but that of copolyamide 6/PXD.6 decreases as the comonomer content increases. Since the 6.6 unit has similar structure with 6 unit in amorphous region, it may not influence the mobility of amorphous chain. However the phenyl ring of PXD.6 unit may reduce the mobility of amorphous chain, and thus the shrinkage in this range decreases.

Fig.5 shows the effect of comonomer content on the thermal shrinkage coefficients of Region 2. In Region 2, the intermediate temperature region between T_g and T_m , shrinkage is also due to the relaxation of oriented amorphous chains as in the Region 1. However the energy barrier for the chain segments which shrink in this range is higher than that of Region 1. Reorganization, chain folding, recrystallization, and general perfecting of the polymer structure take place from the relaxed amorphous region in this range.¹⁷ There-

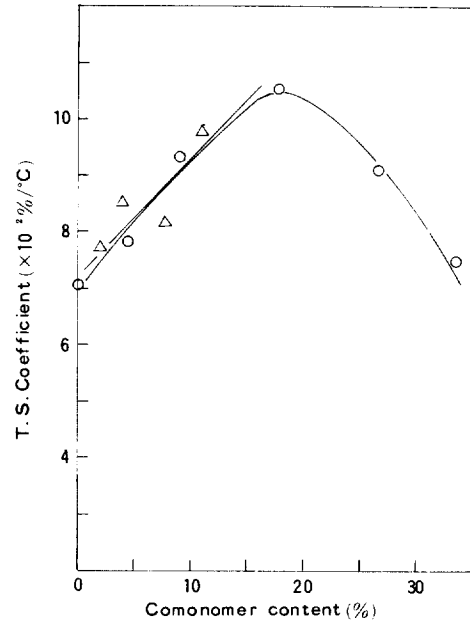


Fig. 6. Effect of comonomer content on the thermal shrinkage coefficient of Region 3 for the draw ratio of 3.0: (○)copolyamide 6/6.6; (△)copolyamide 6/PXD.

fore, the thermal shrinkage coefficients of Region 2 shows the same tendency as in the case of Region 1. But the values are lower than that of Region 1. The lessened shrinkage in this temperature region may be due to the decrease in the population of the energy barrier distribution in this range between amorphous and crystalline shrinkage region.³

Fig.6 shows the effect of comonomer content on the thermal shrinkage coefficient of Region 3. The shrinkage of Region 3 is mainly due to the weakening of the hydrogen bonds in oriented crystalline region and the chain segments directly connected with it, and the effect of amorphous region is also included.

The comonomer units can reduce crystallite size, act as defects in crystallites, and distort crystal lattice. Hence, they can reduce the overall stability of crystalline region. Therefore, the increase of comonomer content may increase the shrinkage in this high temperature range. The decrease of thermal shrinkage coefficient at relatively high comonomer content may be due

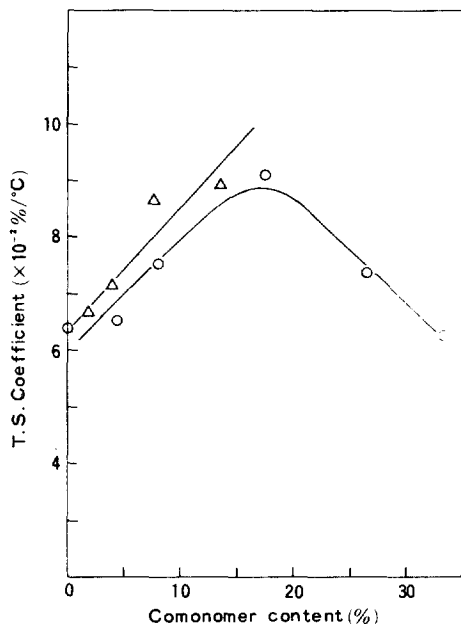


Fig. 7. Effect of comonomer content on the thermal shrinkage coefficient of Region 3 for the draw ratio of 3.0: (○)copolyamide 6/6,6; (△)copolyamide 6/PXD,6.

to the considerable decrease in crystallinity.

As shown in Fig.7, the difference between 6/6,6 and 6/PXD,6 not clear in Fig.6 is shown more clearly when examined the thermal shrinkage coefficients of Region 3 for draw ratio of 3.5. With increasing comonomer content, the thermal shrinkage coefficients of 6/PXD,6 increase more rapidly than those of 6/6,6. Because the structure of PXD,6 unit is more different from the structure of 6 unit than the structure of 6,6 unit, PXD,6 unit may reduce the stability of crystalline region more significantly than 6,6 unit does. Consequently, the shrinkage of 6/PXD,6 in high temperature range increase more rapidly than those of 6/6,6 with increasing comonomer content. It is known that Region 4, so called the highest temperature shrinkage region, reflects the hydrogen-bonding weakening and the initiation of crystalline melting.

Fig.8 shows that the thermal shrinkage coefficient of Region 4 increase with increasing comonomer content. The reason for this behavior

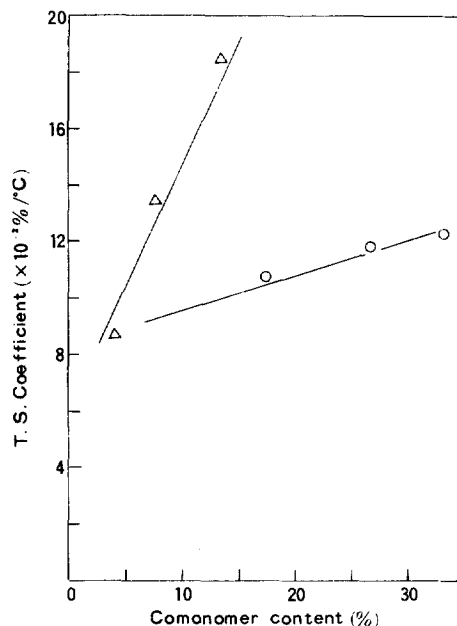


Fig. 8. Effect of comonomer content on the thermal shrinkage coefficient of Region 4 for the draw ratio of 3.0: (○)copolyamide 6/6,6; (△)copolyamide 6/PXD.

is owing to the significant decrease of the stability in crystalline region as in the case of Region 3.

In Fig.9, the temperature of inflection point T1 shows no significant dependence on the comonomer content. The effect of comonomer unit on the amorphous region can not be explained from this result and it may be explained from the peak temperature of the first derivative curve. In Fig.10, the temperature of the inflection point T2 shows no change with 6,6 unit content but shows increase with increasing PXD,6 unit content. T2 is the inflection point between Region 2 and Region 3, and the shrinkage of Region 2 is due to amorphous region and the effect of amorphous region also exists in Region 3. Therefore, temperature of T2 increases with increasing PXD,6 unit content since PXD,6 unit reduce the mobility of amorphous chain.

In Fig.11 the temperature of inflection point T3 shows decrease with increasing comonomer content. T3 is the starting point of slope 4 from

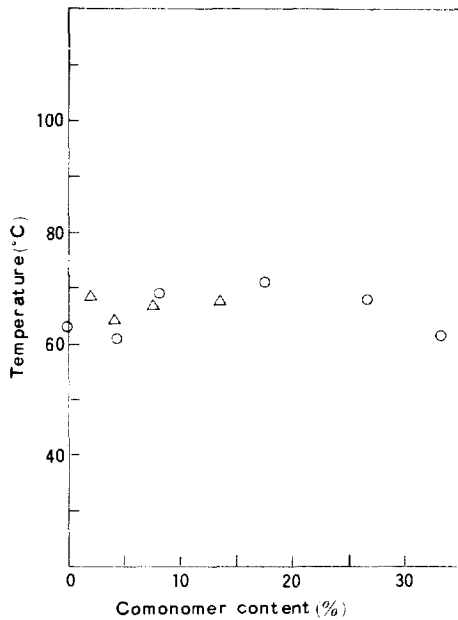


Fig. 9. The temperature of the inflection point T1 versus comonomer content for the draw ratio of 3.0 : (○)copolyamide 6/6.6 ; (△)copolyamide 6/PXD.6.

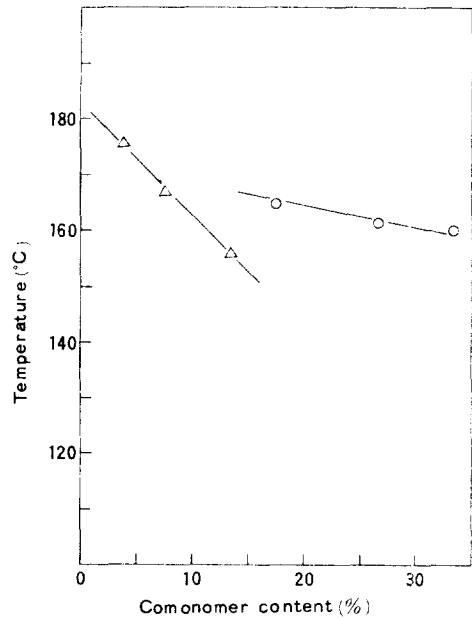


Fig. 11. The temperature of the inflection point T3 versus comonomer content for the draw ratio of 3.0 : (○)copolyamide 6/6.6 ; (△)copolyamide 6/PXD.6.

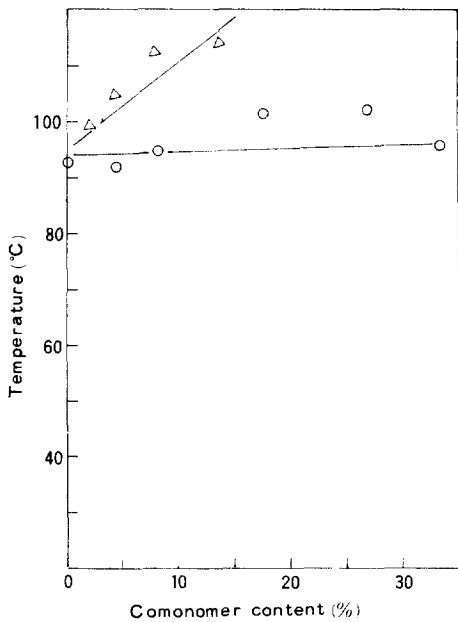


Fig. 10. The temperature of the inflection point T2 versus comonomer content for the draw ratio of 3.0 : (○)copolyamide 6/6.6 ; (△)copolyamide 6/PXD.6.

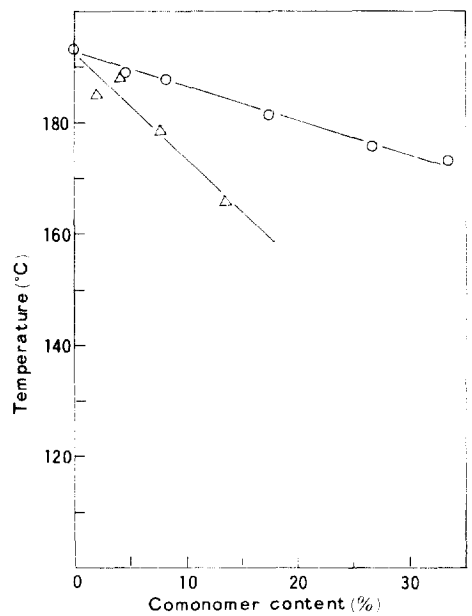


Fig. 12. The temperature of the maximum shrinkage point T4 versus comonomer content for the draw ratio of 3.0 : (○)copolyamide 6/6.6 ; (△)copolyamide 6/PXD.6.

which the massive rupture of hydrogen bonds in crystalline region starts. With increasing comonomer content, the stability of crystalline region decreases and thus the temperature of T3 decreases. For 6/PXD.6, the decreasing tendency is more significant than that for 6/6.6, since PXD.6 unit reduces the stability of crystalline region more largely.

The effect of comonomer content on the temperature of the maximum shrinkage point T4 for draw ratio 3.0 is shown in Fig.12. T4 is related to the melting point of crystalline region and thus decreases with increasing comonomer content as in the case of T3.

CONCLUSIONS

Two series of copolyamides are found to form random copolymers. The thermal shrinkage of copolyamide 6/6.6 at low temperature range does not change significantly with increasing 6.6 unit content because the 6.6 unit is similar to the 6 unit in amorphous region. But the thermal shrinkage of copolyamide 6/PXD.6 at low temperature range decreases with increasing PXD.6 unit content because the aromatic ring of PXD.6 unit may restrict the chain mobility in amorphous region. The thermal shrinkage of copolyamides at high temperature range increases with increasing comonomer content because the stability of the crystalline region decreases with increasing comonomer content. This effect is more significant for copolyamide 6/PXD.6 because the PXD.6 unit is more different than 6.6 unit from 6 unit.

REFERENCES

1. G. M. Bhatt and J. P. Bell, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 575(1976).
2. A. Ribnick, *Text. Res. J.*, **39**, 428(1969).
3. D. R. Buchanan and G. L. Hardegree, *Text. Res. J.*, **47**, 732(1977).
4. T. Pakula and M. Trznadel, *Polymer*, **26**, 1011(1985).
5. M. Trznadel, T. Pakula and M. Kryszewski, *Polymer*, **26**, 1019(1985).
6. P. F. Dismore and W. O. Statton, *J. Polym. Sci., Part C*, **13**, 133(1966).
7. J. H. Dumbleton and D. R. Buchanan, *J. Polym. Sci., Part A-2*, **6**, 1527(1968).
8. D. R. Buchanan and J. H. Dumbleton, *J. Polym. Sci., Part A-2*, **7**, 1113(1969).
9. W. O. Statton, J. L. Koenig and M. Hannon, *J. Appl. Phys.*, **41**, 4290(1970).
10. J. H. Dumbleton, *J. Polym. Sci., Part A-2*, **7**, 667(1969).
11. J. H. Dumbleton, *Polymer*, **10**, 539(1969).
12. J. H. Dumbleton, *Text. Res. J.*, **70**, 1035(1970).
13. R. J. Samuels, *J. Polym. Sci., Part A-2*, **10**, 781(1972).
14. M. P. W. Wilson, *Polymer*, **15**, 277(1974).
15. W. H. Jo and D. H. Baik, *Polymer(Korea)*, **9**, 382(1985).
16. A. Anton, *Text. Res. J.*, **43**, 524(1973).
17. M. Jaffe, in "Thermal Characterization of Polymeric Materials(A. Turi, ed.)", Academic Press, New York(1983).