Anionic Polymerization of *N*-Phenylitaconimide

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ABSTRACT: *N*-Phenylitaconimide (*N*-PII) can be readily polymerized with basic initiators that involve carbide, nitride, and oxide anions such as *sec*-butyllithium, lithium diethylamide, and alkali metal *tert*-butoxide. Poly(*N*-PII) was obtained in 84, 73, and 78% yields with *sec*-butyllithium, lithium diethylamide, and lithium *tert*-butoxide, respectively, in THF at 0 °C for 3 h polymerization. The effect of countercation size on the anionic polymerization rate of *N*-PII (1,1-disubstituted ethylene type monomer with cyclic imide structure) with alkali metal *tert*-butoxides is inverse to that of *N*-phenylmaleimide (*N*-PMI) (1,2-disubstituted ethylene type one); i.e., it was observed that the polymerization rate increased as the ion radius of a countercation decreased. NMR spectroscopic data and molecular orbital calculations suggest that the anionic polymerization of *N*-PII took place only at the vinylidene group and no appreciable side reaction would occur. In the case of using the initiators with Li^+ as a countercation, the molecular weight distribution of poly(*N*-PII) is apparently unimodal and polydispersity is relatively small. The mechanism of the anionic polymerization of *N*-PII was discussed in detail. The thermal properties of poly(*N*-PII) obtained were also presented: it possessed a T_g under its decomposition temperature and could form a film by the cast method while those could not be observed for poly(*N*-PMI).

Introduction

Monomers with a cyclic imide structure have unusual and interesting reactivities for polymerization.[1] *N*-Substituted maleimide which is a monomer possessing the double bond inside the imide ring can be polymerized with radical initiators[2] though they have a 1,2-disubstituted ethylene structure which is usually difficult to polymerize except in a few cases such as fluorine-substituted ones.

In anionic polymerization, *N*-phenylmaleimide which is an *N*-substituted maleimide is polymerized with living character initiated with the *tert*-butoxide anion while it has two carbonyl groups in the vicinity of a carbon−carbon double bond. Possible side reactions such as nucleophilic addition or nucleophilic acyl substitution type reactions cannot occur at the carbonyl group.[3] Owing to the cyclic imide structure in an *N*-substituted maleimide, the reactivity of the internal double bond to the anion may be enhanced while the electrophilicity of carbonyl groups in the imide ring can be reduced.[3,4]

N-Substituted itaconimide with a 1,1-disubstituted ethylene type structure is another monomer with a cyclic imide having a carbon−carbon double bond directly attached outside the imide ring. 1,1-Disubstituted ethylene type monomers are supposed to be more reactive in the polymerization than 1,2-disubstituted ones because of relief of steric hindrance.

Several works, mainly focused on radical polymerization of *N*-substituted itaconimides, have been carried out and published elsewhere.[5−8] However, no work on the anionic polymerization of those monomers has been done in terms of polymer chemistry except that merely intended for polymer synthesis alone.

Polymer obtained from a monomer with a cyclic imide structure is known to be a thermostable organic material but often has problems when processing due to excessive rigidity of the main chain, as observed for poly(*N*-substituted maleimide) that has no T_g below its decomposition temperature[4] and is also too brittle to form films.[9] Investigations of thermal and other properties of poly(*N*-PII) obtained from the anionic polymerization has not yet been carried out either, at least, from a structural viewpoint.

In this paper, detailed studies of anionic polymerization of *N*-phenylitaconimide (*N*-PII): the feature of the anionic polymerization of *N*-PII as a 1,1-disubstituted ethylene type monomer of cyclic imide structure with the outer carbon−carbon double bond and its anionic polymerization mechanism are discussed in detail in connection with the anionic polymerization of *N*-PMI as a 1,2-disubstituted type cyclic imide monomer.

The thermal properties, solubility, and behavior for film formation of poly(*N*-PII) are also described and compared with those of poly(*N*-PMI).

Experimental Section

All experiments related to polymerization were carried out under a purified nitrogen atmosphere in order to exclude oxygen and moisture.

Reagents. Itaconic anhydride and aniline were used as received. Lithium *tert*-butoxide, potassium *tert*-butoxide, toluene, and THF were purified in the same way as described in a previous paper.[3,4,10−13] Cesium *tert*-butoxide was synthesized from 2-methyl-2-propanol with cesium metal. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. *sec*-Butyllithium, phenyllithium, and ethylmagnesium bromide were used after determination of the concentrations of the active species by alkalimetry. Diethylzinc was purified by distillation under reduced pressure (52 °C/50 mmHg) in a nitrogen atmosphere. Lithium diethylamide was used as received.

Synthesis of *N*-Phenylitaconimide (*N*-PII). *N*-PII was prepared by a modified method for the synthesis of *N*-phenylmaleimide (*N*-PMI).[14,15] In a 1 L three-necked flask provided with a stirrer, a reflux condenser, and a dropping funnel were placed 112 g (1 mol) of itaconic anhydride and 400 mL of diethyl ether. The ether solution (100 mL) of aniline (91 mL (1 mol)) was added to the flask through the dropping funnel. The resulting suspension was stirred for 1 h at room temperature and then cooled to 10−15 °C in an ice bath. The white powder was collected by suction filtration (yield: 160 g). To the mixture of 400 mL of acetic anhydride and 30 g of anhydrous sodium acetate was added the powder obtained

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Table 1. Anionic Polymerization of *N*-PII with Alkali Metal *tert*-Butoxides[a]

initiator	solvent	temp (°C)	yield (%)
t-C_4H_9OLi	THF	−78	75
t-C_4H_9OLi	THF	0	78
t-C_4H_9OLi	toluene	0	34
t-C_4H_9ONa	THF	−78	70
t-C_4H_9OK	THF	−78	66
t-C_4H_9OK	THF	0	60
t-C_4H_9OK	toluene	0	41
t-C_4H_9OCs	THF	−78	59
t-C_4H_9OCs	THF	0	75

[a] [*N*-PII] = 2.5×10^{-1} mol/L, [alkali metal *tert*-butoxides] = 5.14×10^{-3} mol/L; polymerization time 3 h.

above, and the resulting mixture was stirred over a steam bath for 30 min. The reaction mixture was cooled to room temperature and then poured into a large amount of ice water. The product precipitated was collected by suction filtration, washed three times with ice-cold water and once with petroleum ether, and dried. Recrystallization from isopropyl ether gave white crystals. Yield: 17.4 g (12% after recrystallization). Mp: 94.5−95.5 °C. ^{1}H NMR is shown in Figure 2A.

Polymerization. Polymerization was carried out in a sealed ampule which was carefully flame dried. After a definite time, the polymer was isolated by precipitation from a mixture of ether/methanol (3/1 (v/v)), washed with methanol three times, and then dried thoroughly below 20 °C in vacuo. The structure of the resulting poly(*N*-PII) was confirmed by ^{1}H NMR and IR.

Measurements. The ^{1}H NMR spectrum was recorded on a JEOL GSX-270 FT-NMR spectrometer using deuterated methyl sulfoxide or chloroform as a solvent. The IR spectrum was measured on a JASCO IR-700 spectrometer. GPC was measured with a TOSOH HLC-802A apparatus at 38 °C with TSK gel G40000HXL−G3000HXL−G2000HXL column series using THF as eluent (flow rate 1.0 mL/min). The molecular weight measured by GPC was calculated from the calibration curve for polystyrene. DSC and TGA measurements were carried out with a DSC 910S differential scanning calorimeter and TGA 51 thermogravimeter, respectively, with Thermal Analyst 2000 (TA instruments), under a nitrogen atmosphere with a heating rate of 10 deg/min.

Molecular Orbital (MO) Calculation. MO calculation was carried out by PM3[16] in MOPAC ver. 6[17] which is from CAche Scientific, Inc.

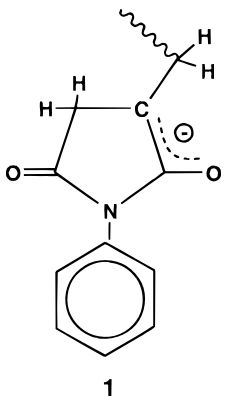
Results and Discussion

Reactivity of *N*-PII for Anionic Initiators. The results of anionic polymerization of *N*-PII with alkali metal *tert*-butoxides for 3 h are summarized in Table 1. *N*-PII is readily polymerized with alkali metal *tert*-butoxides as well as *N*-PMI. Lithium *tert*-butoxide was the most active initiator to afford poly(*N*-PII) in 75% yield even for 3 h polymerization time at −78 °C in THF. The fact that the alkoxide ion which is a relatively weaker base than the carbanion can initiate anionic polymerization indicates that the vinylidene group of *N*-PII becomes more susceptible to initiators used for anionic polymerization than that of methyl methacrylate probably due to the cyclic imide structure bearing carbonyl groups.

The effect of the countercation on the anionic polymerization of *N*-PII, which is the 1,1-disubstituted ethylene type monomer with cyclic imide structure, is different from that of the anionic polymerization of *N*-PMI, which is the 1,2-disubstituted ethylene type one. For *N*-PMI, the polymerization yield increased as the ion radius of the countercation increased: for instance, lithium *tert*-butoxide gave approximately a 10% yield of poly(*N*-PMI) in THF at −72 °C after 3 h polymerization, whereas an almost quantitative yield was obtained with potassium *tert*-butoxide. In contrast with these results, poly(*N*-PII) was produced in very high yield (75%) with lithium *tert*-butoxide in THF at −78 °C for 3 h in the anionic polymerization of *N*-PII, but when using cesium *tert*-butoxide as an initiator, the polymer yield was relative low (59%) under the same condition. The yields of poly(*N*-PII) with sodium and potassium *tert*-butoxides (70 and 66%, respectively) lie between those obtained with lithium and cesium *tert*-butoxides.

The positive correlation of the propagation rate with the countercation size was observed for the anionic polymerization of styrene with alkali metal naphthalenide in THF,[18−20] while a negative correlation was observed for the anionic polymerization of *N*-PMI with alkali metal *tert*-butoxides in THF[13] and styrene with alkali metal naphthalenide in dioxane of a lower polar solvent.[21] The propagation rate can be related to the polymerizations yield at a definite time in the present case, because the polymerizations were carried out under the same conditions other than the types of countercations of the initiators.

For the anionic polymerization of *N*-PII with alkali metal *tert*-butoxides in THF, the positive correlation of the propagation rate which can be shown in terms of the polymerization yield with the countercation size is observed as illustrated in Figure 1. This implies that in the propagation stage of the anionic polymerization of *N*-PII is different in the transition state from that of *N*-PMI. The geometry of the reaction species in the transition state—the spatial orientation mode among the propagating anion, countercation, and monomer—should be different between anionic polymerizations of *N*-PII and *N*-PMI because, as shown below, the structure of the negative charged carbon of the propagating species, which is the reactive center of the enolate anion, is different between that of *N*-PII (tertiary (**1**)) and of *N*-PMI (secondary (**2**)) in the anionic polymerization.



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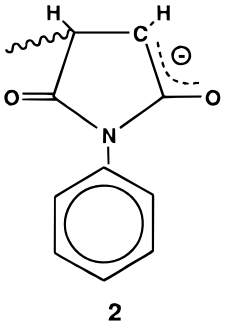

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The results of anionic polymerization of *N*-PII with other anionic initiators are shown in Table 2. Poly(*N*-PII) was obtained in high yield with the initiators for anionic polymerization evolving the carbanion such as *sec*-butyllithium and phenyllithium which might give rise to abstraction of methylene protons in the imide ring being α to the position of the carbonyl group. Lithium diethylamide (which evolves the N^- anion) and ethylmagnesium bromide—a Grignard reagent having low activity as an initiator for the anionic polymerization of *N*-PMI—also afforded poly(*N*-PII) in good yield as well as lithium *tert*-butoxide.

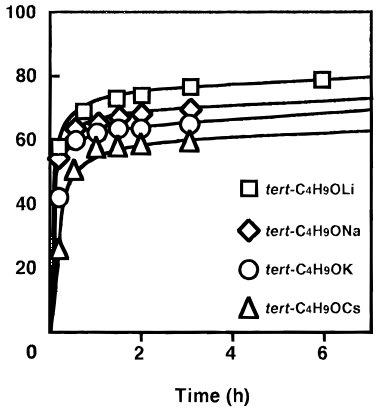

Figure 1. Time−conversion curves of anionic polymerization of *N*-PII with various alkali metal *tert*-butoxides: (□) lithium *tert*-butoxide; (◇) sodium *tert*-butoxide; (○) potassium *tert*-butoxide; (△) cesium *tert*-butoxide. [*N*-PII] = 2.5 × 10^{-1} mol/L, [alkali metal *tert*-butoxide] = 5.14 × 10^{-3} mol/L, in THF at −78 °C.

Table 2. Anionic Polymerization of *N*-PII with Other Anionic Initiators[a]

initiator	solvent	temp (°C)	time (h)	yield (%)
s-C_4H_9Li	THF	0	3	84
s-C_4H_9Li	toluene	0	3	26
C_6H_5Li	THF	0	3	90
C_6H_5Li	toluene	0	3	19
$(C_2H_5)_2NLi$	THF	−78	3	86
$(C_2H_5)_2NLi$	THF	0	3	73
$(C_2H_5)_2MgBr$	THF	0	3	82
$(C_2H_5)_2MgBr$	toluene	0	3	59
$(C_2H_5)_2Zn$	THF	60	24	78

[a] [*N*-PII] = 2.5 × 10^{-1} mol/L, [initiator] = 5.14 × 10^{-3} mol/L.

As a polymerization solvent, polar THF is better than a nonpolar solvent such as toluene for all anionic initiators at low polymerization temperatures (below 0 °C).

Mechanism of the Anionic Polymerization of *N*-PII. The structure of poly(*N*-PII) obtained and the reaction mode of the anionic polymerization of *N*-PII were analyzed by ^1H and ^{13}C NMR. Figure 2 depicts the ^1H NMR of poly(*N*-PII) obtained with lithium *tert*-butoxide and the *N*-PII monomer. In the ^1H NMR spectrum the two peaks seen at 5.71 and 6.44 ppm, where weak long distance spin−spin couplings were observed, assignable to vinylidene protons of the *N*-PII monomer (relative signal intensity: 1H and 1H, respectively), have completely disappeared, and a new singlet peak is observed at 2.01 ppm with the relative signal intensity of 2H in the spectrum of poly(*N*-PII). Furthermore, a signal assignable to methylene protons in the imide ring observed at 3.48 ppm for the monomer *N*-PII, which was also with weak long distance spin−spin couplings, was shifted upfield and appears at 2.63 ppm for poly(*N*-PII) maintaining its relative signal intensity (2H). A signal due to the initiator fragment is observed at 0.76 ppm.

The average degree of polymerization of the poly(*N*-PII) calculated from the signal intensities of the phenyl group and the *tert*-butyl group (initiator fragment) is 40, which is a little larger but tolerable considering experimental error when compared with the theoretical value ($\overline{DP}$ = 37) estimated from the conversion and the feed ratio of the monomer to the initiator.

For the ^{13}C NMR spectra, the sp^2 vinylidene carbon in the *N*-PII monomer observed at 121.5 ppm has

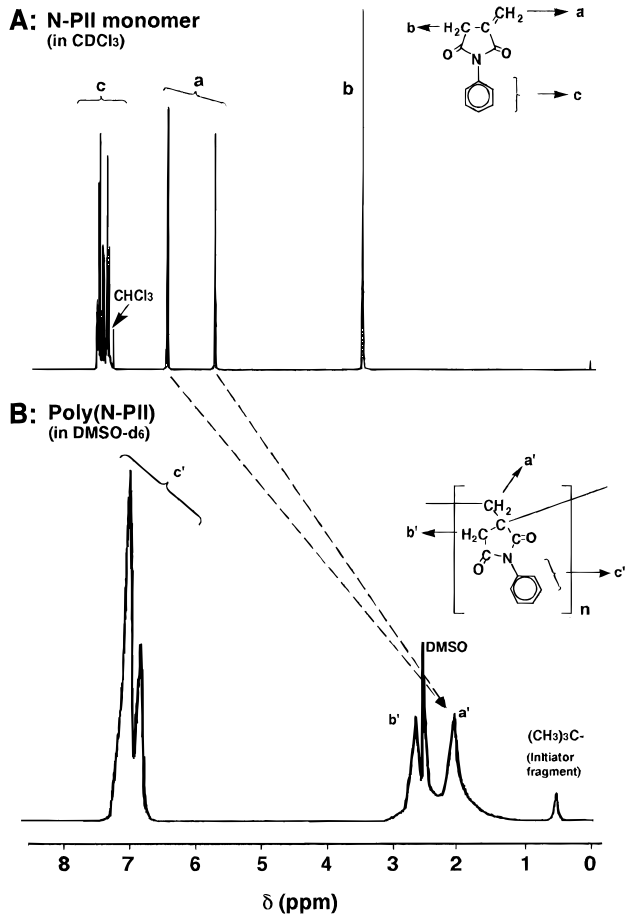

Figure 2. ^1H NMR of *N*-PII in $CDCl_3$ (A) and poly(*N*-PII) with *t*-C_4H_9OLi in DMSO-d_6 (B).

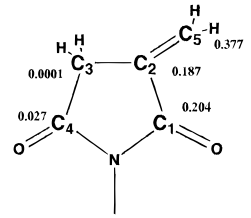

Figure 3. LUMO densities of each carbon of *N*-PII.

disappeared and changed to the sp^3 main chain methylene carbon in poly(*N*-PII) recorded at 46.1 ppm.

Other samples of poly(*N*-PII) obtained under different conditions using different initiators or solvents gave the same NMR spectra other than the signal due to the initiator fragment.

These results indicate that the anionic polymerization of *N*-PII takes place only at the vinylidene group and no appreciable side reaction such as the nucleophilic addition or substitution at the carbonyl carbon or the abstraction of the α-hydrogen next to an imide carbonyl group occurs in this anionic polymerization system, since signals due to side reactions could not be detected.

Results of the molecular orbital calculation support this anionic polymerization behavior of *N*-PII. LUMO densities of each carbon in the *N*-PII monomer except the phenyl ring are shown in Figure 3. The LUMO density of the β-carbon in the vinylidene group (0.377 (**C_5**)) is higher than those of the carbonyl carbons (0.204 (**C_1**) and 0.027 (**C_4**)). It is remarkable that the LUMO density of the carbonyl carbon in the imide ring with less steric hindrance (**C_4**) is considerably lower when

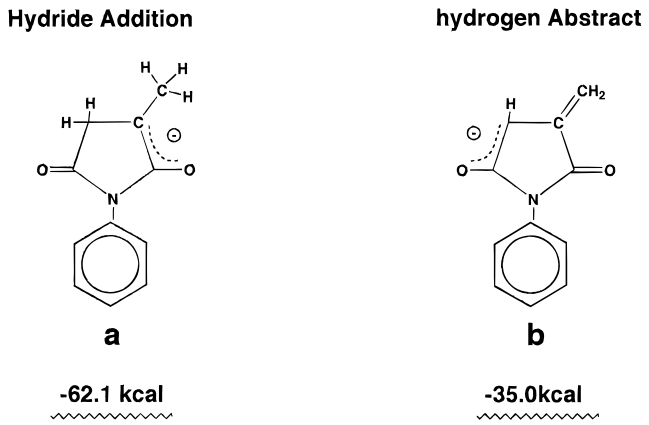

Figure 4. Structures of the enolate anion forming in *N*-PII: hydride addition to the β-carbon of the vinylidene group (a); hydrogen abstraction from the α-position (b). The heat of formation calculated by the PM3 method is given below each structure.

compared to that of $\mathbf{C_5}$. This indicates that for the reaction of *N*-PII with a nucleophile, the nucleophilic addition to the $\mathbf{C_5}$ carbon in the vinylene group is much preferred to nucleophilic addition or substitution at the carbonyl carbon as side reactions of the anionic polymerization.

The two types of enolate anions that could be taken into account for the reaction of *N*-PII with a nucleophile are illustrated in Figure 4. One is from the hydride addition to the β-carbon of the vinylidene group (**a**), which is a model for the propagating species of the anionic polymerization, and the other is from the abstraction of an α-hydrogen next to an imide carbonyl group (**b**), which is a model for a second side reaction. The enolate anion of the structure **a** is considered to be more stable and readily formed than that of **b** because the enol form for **a** has the double bond that has the greater number of substituents. The normal anionic polymerization reaction that proceeds through the **a** type enolate anion would be, thus, much preferred to α-hydrogen abstraction as a side reaction. The values of heat of formation calculated by the PM3 method for each structure of the enolate anions, also shown in Figure 4 (−62.1 kcal/mol for **a** and −35.0 kcal/mol for **b**), support this conclusion.

Figure 5 shows the molecular weight distributions of poly(*N*-PII) obtained with alkali metal *tert*-butoxides with different cation sizes. Interestingly, the molecular weight distribution appears differently due to the countercation size. In the case of the lithium ion as a countercation with which anionic polymerization of *N*-PII proceeds most rapidly, the molecular weight distribution of poly(*N*-PII) is apparently unimodal. The number average molecular weight calculated by using the calibration curve for polystyrene is 7.6×10^3 ($\overline{DP} = 41$). This fairly agrees with the value obtained from the ^{1}H NMR signal intensities and the theoretical value calculated from the data in Table 1 described earlier. The polydispersity ($\bar{M}_w/\bar{M}_n = 1.3$) is also relatively small. On the other hand, the molecular weight distributions of poly(*N*-PII) obtained by the anionic polymerization with larger countercations such as potassium or cesium ion are bimodal. The high molecular weight part appears on the chromatograms, and it increases with the countercation size. The polydispersities for those poly(*N*-PII) are 2.4 and 5.0 for potassium and cesium cations, respectively. The number average molecular weights, however, do not deviate from the theoretical

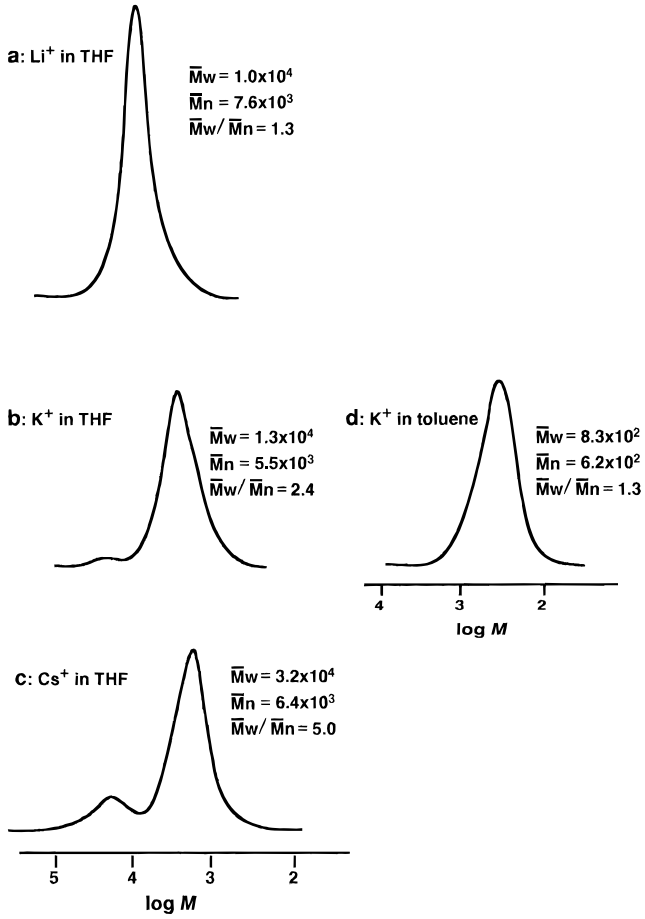

Figure 5. Molecular weight distribution of poly(*N*-PII) with various alkali metal *tert*-butoxides: (a) with *t*-C_4H_9OLi; (b) with *t*-C_4H_9OK; (c) with *t*-C_4H_9OCs, in THF, at −78 °C; (d) with *t*-C_4H_9OK, in toluene, at 0 °C.

values calculated from the data in Table 1 (6.0×10^3 for the potassium cation and 5.4×10^3 for the cesium cation). This result indicates that two kinds of propagating ionic species take part in the propagating step of the anionic polymerization of *N*-PII as the countercation size increases.

The propagating ionic species of the anionic polymerization is classified into two types; i.e., one is called a free ion and the other is called a contact ion pair. For the anionic polymerization of *N*-PMI in THF, the propagating stage is dominated by the contact ion pair.[12,13]

However, for the anionic polymerization of *N*-PII, the propagation by free ion type growing species probably cannot be disregarded when the countercation size becomes larger. The enolate with a tertiary (trisubstituted) carbanion formed in the propagating species of the anionic polymerization of *N*-PII is sterically more crowded than that with a secondary (disubstituted) carbanion in the propagating species of the anionic polymerization of *N*-PMI. As the countercation becomes larger, therefore, it is more difficult for the propagating species of the anionic polymerization of *N*-PII in THF to form only contact ion species, while solvation of the countercation with solvent molecules can occur to some extent, competing against that with the enolate anion. This consideration is supported by the result that the molecular weight distribution of poly(*N*-PII) obtained by anionic polymerization with potassium *tert*-butoxide in toluene shows a unimodal feature, whereas the propagation of the anionic polymerization is dominated

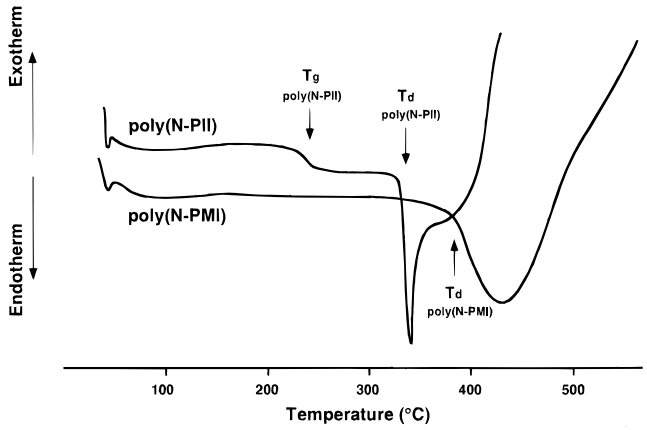

Figure 6. DSC curves of poly(*N*-PII) and poly(*N*-PMI) obtained with lithium *tert*-butoxide at −78 °C in THF, measured under a nitrogen atmosphere with a heating rate of 10 deg/min.

by the contact ion pair since toluene as a less polar solvent cannot solvate sufficiently the countercation.

Thermal Properties and Solubility of Poly(*N*-PII). Figure 6 shows DSC curves of poly(*N*-PII) and poly(*N*-PMI) obtained with lithium *tert*-butoxide. It is observed that poly(*N*-PII) possesses T_g at 236 °C,[22] while poly(*N*-PMI) has no T_g below its decomposition temperature (T_d: 375 °C). The result of TGA analysis revealed that poly(*N*-PII) began to decompose at 331 °C and the 5% weight loss temperature was 350 °C. The TGA curve became almost flat near 600 °C at around 20% of weight remaining, and carbon black was recovered from the sample container after the measurement. The fact that T_g exists below T_d suggests that poly(*N*-PII) is a thermoplastic polymer in contrast with poly(*N*-PMI) which cannot be processed.

The solubility of poly(*N*-PII) is a little different from that of poly(*N*-PMI) possessing another cyclic imide structure. Poly(*N*-PII) was, for example, soluble in acetone in addition to the solvents which could dissolve poly(*N*-PMI).

Poly(*N*-PII) could also form a film on glass from its acetone or THF solution by the cast method under the condition that solvent was evaporated very slowly and carefully, while no film was able to be formed from a THF solution of poly(*N*-PMI) in the same way.

References and Notes

(1) Hargreaves, M. K.; Pritchard, J. G.; Dave, H. R. *Chem. Rev.* **1970**, *70*, 439.
(2) Cubbon, R. C. P. *Polymer* **1965**, *6*, 419.
(3) Hagiwara, T.; Shimizu, T.; Someno, T.; Yamagishi, T.; Hamana, H.; Narita, T. *Macromolecules* **1988**, *21*, 3324.
(4) Hagiwara, T.; Someno, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1011.
(5) Oishi, T. *Polym. J.* **1980**, *12*, 719.
(6) Oishi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1053.
(7) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Br. Polym. J.* **1990**, *23*, 353.
(8) Sato, T.; Morino, K.; Tanaka, H.; Ota, T. *Eur. Polym. J.* **1989**, *25*, 1281.
(9) Hagiwara, T.; Yanaba, N.; Takada, T.; Hamana, H.; Narita, T. *Polym. Bull.* **1991**, *26*, 503.
(10) Hagiwara, T.; Mizota, J.; Hamana, H.; Narita, T. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 169.
(11) Hagiwara, T.; Sato, J.; Hamana, H.; Narita, T. *Makromol. Chem.* **1985**, *188*, 1825.
(12) Hagiwara, T.; Shimizu, T.; Uda, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 185.
(13) Hagiwara, T.; Shimizu, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2437
(14) Searle, N. E. U.S. Patent 244536, 1948; *Chem. Abstr.* **1948**, *42*, 7340c.
(15) Cava, M. P.; Deana, A. A.; Muth, K.; Michell, M. J. *Organic Syntheses*; John Wiley and Sons: New York, 1973; Collect. Vol. No. 5, p 944.
(16) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
(17) MOPAC (QCPE No. 455), developed by J. J. P. Stewart, is a general-purpose semi-empirical molecular orbital package for the study of chemical structures and reactions.
(18) Geacinotov, C.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 2508.
(19) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 612.
(20) Bhattacharyya, D. N.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 624.
(21) Szwarc, M. in *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; John Wiley and Sons: New York, 1973; Vol. II, p 375.
(22) This value is in good agreement with preceding data (T_g = 232 °C): Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 486.

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