ELSEVIER

Polymer 40 (1999) 4049–4054

polymer

Polymerization of *N*-[4-(azidocarbonyl)phenyl]maleimide and *N*-[4-(N'-phenoxycarbonylamino)phenyl]maleimide polymers containing aromatic isocyanate precursors

Ji Young Chang[a,*], Tae Ja Kim[b], Man Jung Han[b], Kyu Ho Chae[c]

[a]*Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, South Korea*
[b]*Department of Applied Chemistry, Ajou University, Suwon 442-749, South Korea*
[c]*Department of Polymer Engineering, Chonnam National University, Kwangju 500-757, South Korea*

Received 23 June 1998; accepted 17 August 1998

Abstract

N-[4-(Azidocarbonyl)phenyl]maleimide (**3**) and *N*-[4-(N'-phenoxycarbonylamino)phenyl]maleimide (**5**) were polymerized and copolymerized with methyl methacrylate (MMA) or acrylic acid (AA) by initiation with AIBN. The resultant polymers were to have aromatic isocyanato groups when heated. In the differential scanning calorimetry measurement, the polymers from monomer **3** showed a strong and broad exotherm around 130°C. Thermogravimetric analysis also showed a weight decrease corresponding to the elimination of nitrogen at that temperature. The formation of isocyanato groups was confirmed by infra-red measurement with varying the cell temperature. The coupling reaction of the polymer with *N*-4-(nitrophenyl)-L-prolinol, resulting in the formation of urethane bonds, was carried out in a quantitative yield. The crosslinked films from copolymers of **5** and MMA or AA were obtained when heated above 200°C. The cured films were insoluble in common organic solvents. With the copolymers with AA it was expected that carboxylic groups would react with isocyanato groups generated from urethane units when heated. The copolymer was degraded above 150°C. After curing, its thermal stability improved dramatically, no weight loss being observed up to 300°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *N*-phenylmaleimide polymer; Isocyanate; Coupling reaction

1. Introduction

Polymers with reactive groups are widely used for the coupling reaction with functional compounds with valuable properties such as catalytic activities, biological activities, and electro-optical properties [1]. They can also undergo crosslinking reactions, resulting in the formation of thermoset polymers. For the coupling reaction, the polymers are usually required to have strong nuclophilicity or electrophilicity. Examples of the former are the polymers having amino groups, e.g. poly(vinyl amine) and polyethylenimine, and hydroxyl groups such as poly(vinyl alcohol). Examples of the latter include polymers having carboxylic groups, which are activated, for example in the form of acyl chloride before the reaction [1].

Isocyanates are well known for their facile reaction with alcohols. This reaction has been successfully utilized in producing polyurethanes. They can also react with amines, carboxylic acids, and water to yield ureas, amides, and amines, respectively [2–4]. Due to their high reactivity towards various nucleophiles, they are expected to show high coupling efficiency, being suitable for the reaction particularly with the bulky compounds such as nonlinear optical (NLO) chromophores or biologically active natural compounds. The linear polymers having isocyanato groups, however, have seldom been prepared probably due to their synthetic difficulties mainly caused by high reactivity of isocyanato groups. This problem may be circumvented by using the monomers with the groups precursory to isocyanato groups for polymerization.

Isocyanates are generally prepared in two ways, one being through decomposition of carbamoyl intermediates, the other one being by carbon to nitrogen migration of *N*-leaving group substituted amides [4]. In this work, we prepared *N*-phenylmalemide polymers with isocyanate precursors, acyl azide and *N*-phenoxyamide groups and their thermal reactions were investigated. *N*-Phenylmaleimide and its derivatives are easily polymerized under the radical polymerization conditions. The resultant polymers are known to exhibit high T_gs due to the rigid imide rings in

---

* Corresponding author.

PII: S0032-3861(98)00600-4

Table 1
Polymerization results of *N*-phenylmalemides

Polymer	M1	M2	[M1] in monomer (%)	Yield (%)	[M1] in copolymer (%)	M_w ($\times 10^3$)	T_g (°C)
6a	**3**	MMA	17	80	12	55[a]	–
6b	**3**	MMA	25	73	21	41[a]	–
6c	**3**	MMA	50	77	34	30[a]	–
7a	**5**	MMA	12	81	10	66[b]	145
7b	**5**	MMA	25	75	20	31[b]	155
7c	**5**	MMA	50	80	50	23[b]	180
8a	**5**	AA	5	78	5	52[b]	–
8b	**5**	AA	10	81	10	41[b]	–
8c	**5**	AA	25	75	20	19[b]	–

[a] Measured by g.p.c. in chloroform, polystyrene standards.
[b] Measured by g.p.c. in THF, polystyrene standards.

the backbones. Because of the feasibility of their radical polymerization and the excellent thermal stability of the resultant polymers, many interesting compounds have been attached to them and their homopolymerization and copolymerization studied extensively [5–8]. Recently we also reported *N*-phenylmaleimides having NLO chromophores through urethane linkages and their radical polymerization to yield a new class of second-order NLO polymers with the much improved thermal stability [9]. The polymers studied in this work were stable at room temperature and by simply heating they were to have aromatic isocyanato groups by decomposition of acyl azide and *N*-phenoxyamide groups, which underwent the coupling reaction or crosslinking reaction leading to the thermoset polymers.

2. Experimental

2.1. Materials and instrumentation

Compounds **1** and **2** were prepared following the procedures in the literature [8]. All reagents were purchased from Aldrich Chemical Co. Maleic anhydride and 2,2′-azobisisobutyronitrile (AIBN) were purifies by recrystallization from benzene and methanol, respectively. Reagent grade solvents were dried and purified as follows. *N*,*N*-Dimethylformamide (DMF) was dried over anhydrous P_2O_5 and purified by distillation. Toluene was distilled over CaH_2. 1,4-Dioxane and tetrahydrofuran (THF) were distilled over Na. The other reagents were used as received. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian-Gemini 200 spectrometer. Infra-red (i.r.) spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. Gel permeation chromatography (g.p.c.) was carried out with a Waters 150°C g.p.c. with a M410 refractive index detector. Thermal analyses were performed by a Dupont 2010 differential scanning calorimeter (d.s.c.) and a 2050 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min under nitrogen.

2.2. Synthesis of N-[4-(azidocarbonyl)phenyl]malemide (**3**)

This compound was prepared from sodium azide (0.65 g, 10.0 mmol) in water (25 ml) and compound **2** (2.07 g, 8.8 mmol) in methylene chloride (35 ml) according to the previous paper [9], in 80% yield (mp 120–121°C).

2.3. Synthesis of N-[4-(N′-phenoxycarbonylamino)phenyl]maleimide (**5**)

This compound was prepared from phenol (0.5 g, 5.3 mmol) and compound **3** (1 g, 4.1 mmol) in the presence of dibutyltin dilaurate (DBTDL, 0.1 ml) in toluene (200 ml) according to the previous paper [9], in 75% yield (mp 206–208°C).

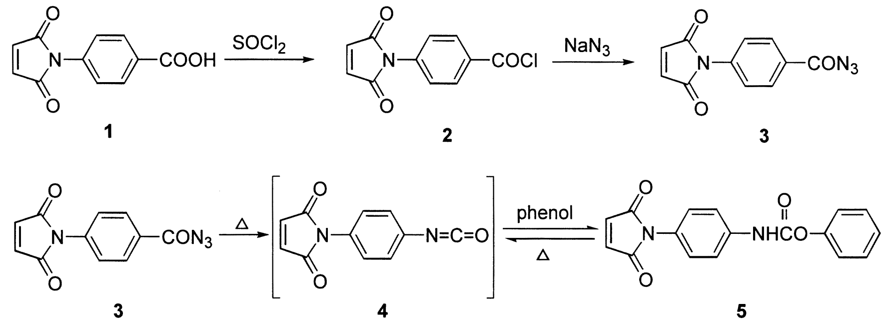
2.4. Homopolymerization of **3**

Typical procedure was as follows: Monomer **3** (1.0 g, 4.1 mmol) and AIBN (10 mg) were dissolved in THF (15 ml). Polymerization was carried out at 60°C for 24 h. After concentration by evaporation of the solvent under reduced pressure, the resulting polymer was isolated by precipitation into methanol and purified by reprecipitation from the chloroform polymer solution into diethyl ether twice (yield 74%).

^{1}H n.m.r. ($CDCl_3$): δ 8.0–8.2, 6.9–7.5 (phenyl protons), 3.6–4.1 (backbone protons). I.r. (KBr, cm^{-1}): 2940, 2144, 1709, 1525, 1393, 1262.

2.5. Copolymerization of **3** with MMA

Typical procedure was as follows: Monomer **3** (0.3 g, 1.23 mmol), appropriate amount of comonomer, for example methyl methacrylate (MMA) (0.40 ml, 3.75 mmol), and AIBN (4.0 mg) were dissolved in THF (6 ml). Polymerization was carried out at 60°C for 24 h. After concentration by evaporation of the solvent under reduced pressure, the resulting polymer was isolated by precipitation into methanol and purified by reprecipitation from the methylene chloride polymer solution into methanol twice. The polymerization results are summarized in Table 1.



Scheme 1.

^{1}H n.m.r. (CDCl$_3$): δ 8.05–8.20, 7.00–7.50 (phenyl protons), 3.5–4.1 (OCH$_3$, CH from monomer **3**), 1.7–2.2 (CH$_2$ from MMA), 0.7–1.6 (CH$_3$ from MMA). I.r. (KBr, cm^{-1}): 2998, 2949, 2143, 1731, 1450, 1260.

*2.6. Copolymerization of **5** with MMA*

Typical procedure was as follows: A solution of monomer **5** (0.2 g, 0.65 mmol), appropriate comonomer, for example MMA (0.49 ml, 4.6 mmol), and AIBN (6 mg) in DMF (3 ml) was charged into a polymerization tube. After freeze–thaw treatments under nitrogen, the tube was sealed under vacuum. Polymerization was carried out at 70°C for 24 h. The resulting polymer was isolated by precipitation into methanol and purified by reprecipitation from the methylene chloride polymer solution into methanol. The polymerization results are summarized in Table 1.

^{1}H n.m.r. (dimethyl sulfoxide-d_6 (DMSO-d_6)): δ 10.4 (NH), 7.1–7.7 (phenyl protons), 3.5–4.0 (OCH$_3$, CH from monomer **5**), 1.5–2.2 (CH$_2$ from MMA), 0.5–1.5 (CH$_3$ from MMA). I.r. (KBr, cm^{-1}): 3445, 3004, 2957, 1738, 1204, 1157.

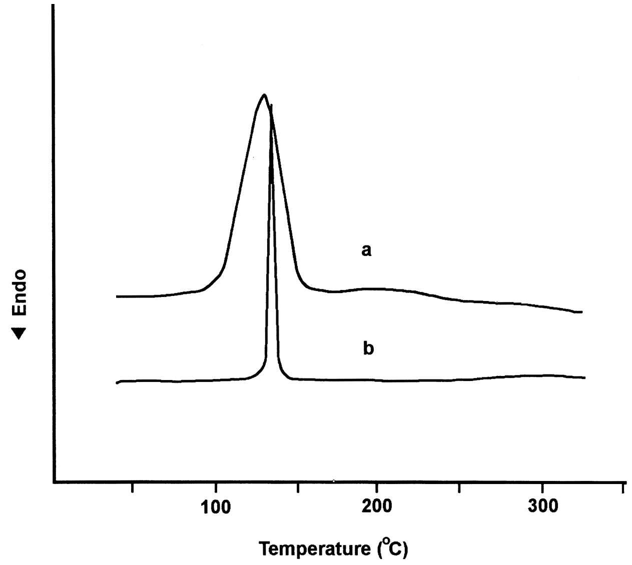


Fig. 1. D.s.c. thermograms of: (a) azide compound **3**; (b) polymer **6a**.

*2.7. Copolymerization of **5** with AA*

Polymerization was carried out at 70°C for 24 h in the same manner as the copolymerization with MMA. The resulting polymer was isolated by precipitation into methylene chloride and purified by reprecipitation from the acetone polymer solution into methylene chloride. The polymerization results are summarized in Table 1.

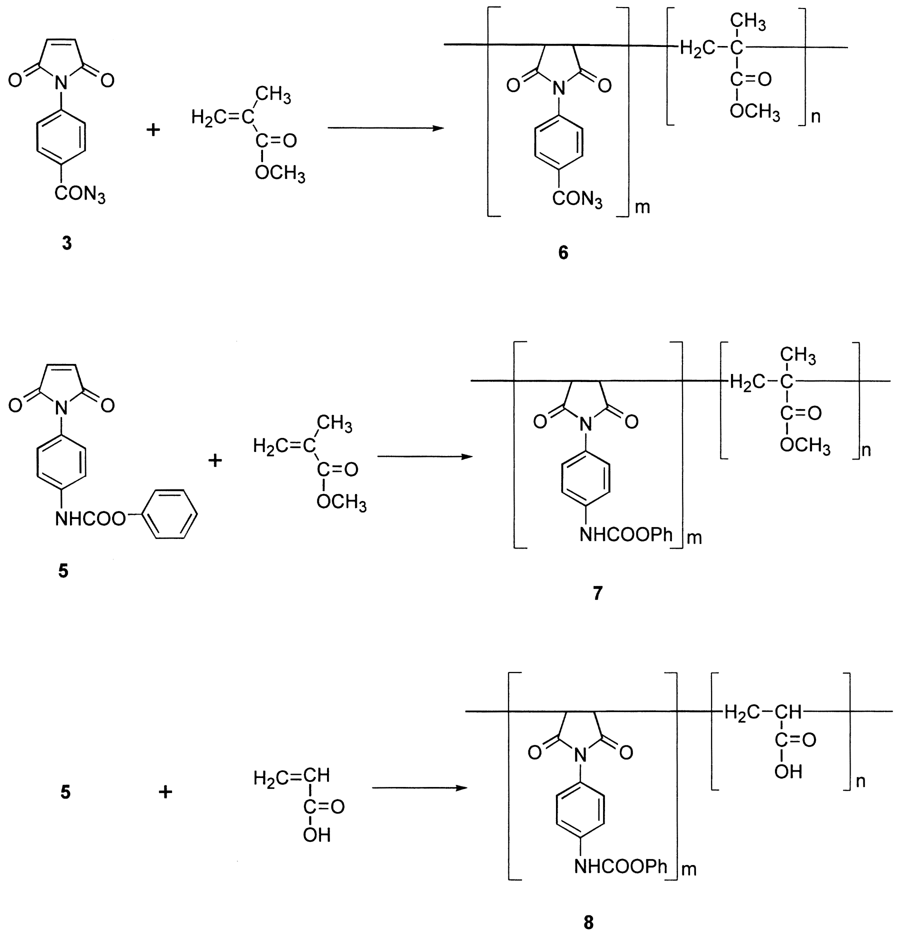
^{1}H n.m.r. (DMSO-d_6): δ 12.2–12.8 (COOH), 10.4 (NH), 7.1–7.6 (phenyl protons), 3.5–4.0 (OCH$_3$, CH from monomer **5**), 1.2–2.4 (backbone protons from AA). I.r. (KBr, cm^{-1}): 3500–3000, 2951, 2604, 1713, 1540, 1413, 1199.

*2.8. Coupling reaction of polymer **6** with NPP*

To a solution of polymer **6b** (0.5 g) in 1,4-dioxane (60 ml) was added *N*-(4-nitrophenyl)-L-prolinol (NPP) (0.8 g, 3.6 mmol) and DBTDL (0.1 ml) at room temperature. The solution was refluxed for 1 h. After concentration by evaporation of the solvent under reduced pressure, the polymer was isolated by precipitation into methylene chloride/methanol (1/9) and purified by reprecipitation from the THF polymer solution into methylene chloride/methanol twice (0.6 g yield).

3. Results and discussion

Monomers **3** and **5** were prepared according to the literature (Scheme 1). As we reported in the previous paper [9], compound **3** was converted to isocyanato compound **4** when heated in toluene at 100°C. D.s.c. showed a very sharp and strong exotherm at 134°C (Fig. 1), corresponding to the elimination of nitrogen from azide groups and subsequent rearrangement to isocyanato groups [10]. The reaction in the presence of phenol gave a urethane (**5**), in which phenol was expected to react with the isocyanato groups immediately after their generating. Phenol was acting as a leaving group as well as a nucleophile. Although it was difficult to isolate compound **4** resulted from the thermal reaction of compound **5**, in the presence of an alcohol as a second nucleophile, the relevant urethane was easily obtained. While the isocyanato group formed by the irreversible reaction with a loss of nitrogen from compound **3**, the



Scheme 2.

thermal reaction of **5** was reversible, with the equilibrium existing.

Functional polymers are often prepared by radical polymerization of the vinyl monomers with functional substituents. Compound **4** was so reactive toward various nucleophiles that the compounds with hydroxyl or amino groups could be attached to it with ease. The resultant products underwent homopolymerization or copolymerization with radical initiators. The radical polymerization, however, often suffers from giving the polymers of low molecular weights when substituents are bulky or have reactive hydrogens. This problem may be overcome by introducing substituents after polymerization via the coupling reaction with a reactive polymer. For efficient coupling reactions, high reactivities of the polymers are required. Unfortunately, the polymerization of compound **4** was not practical for its high reactivity, yielding an insoluble product. As an alternative, compound **3** or **5** could be polymerized to give a precursor polymer. In which isocyanato groups would be generated by simply heating so as to react with nucleophilic functional compounds.

Homopolymerization of compound **3** and its copolymerization with MMA were carried out with AIBN in THF at 60°C (Scheme 2). Above 70°C, partial degradation of the azide groups was observed. The polymerization results are summarized in Table 1. In the copolymerization, the monomer composition was determined by ^{1}H n.m.r. spectroscopy and found to be changed by varying the monomer feed ratios. The polymers were soluble in methylene chloride, chloroform, 1,4-dioxane, THF, DMF, and DMSO.

The polymers showed the similar thermal behaviors to those of compound **3** [10]. In the d.s.c. thermogram, a strong and broad exotherm appeared around 130°C (Fig. 1). TGA also showed a weight decrease corresponding to the elimination of nitrogen at that temperature. This raised an interesting question of whether the same reaction involving a skeleton rearrangement as compound **3** took place when the polymer reaction was considered. To confirm the formation of isocyanato groups, the polymer solutions in THF were cast on a NaCl plate. After drying, they were subjected to i.r. measurement with varying the cell temperature (Fig. 2). At room temperature, the peak for azide groups appeared at 2143 cm^{-1}. As increased the cell temperature above 90°C, the N_3 peak intensity decreased and a new peak corresponding to the stretching of isocyanato groups showed up at 2270 cm^{-1}. The intensity of this peak increased gradually up to 130°C, at which the N_3 peak disappeared completely, then decreased with the temperature

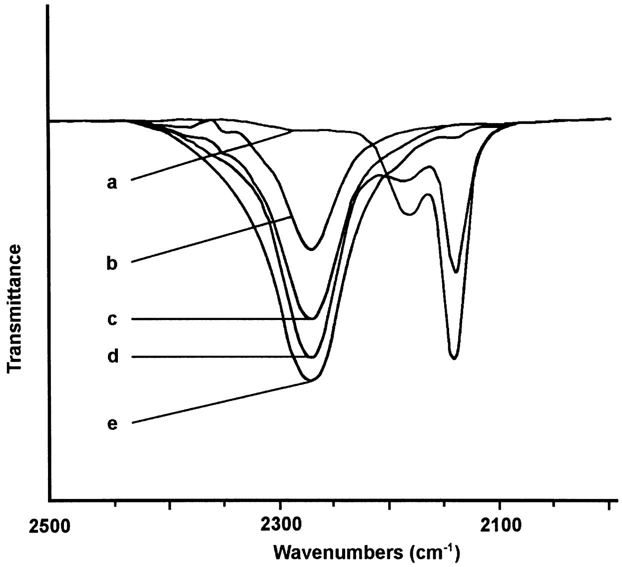


Fig. 2. I.r. spectra of polymer **6a** in a film obtained at: (a) room temperature; (b) 200°C; (c) 150°C; (d) 90°C; (e) 130°C. The temperature was increased from room temperature to 200°C with a rate of 10°C/min.

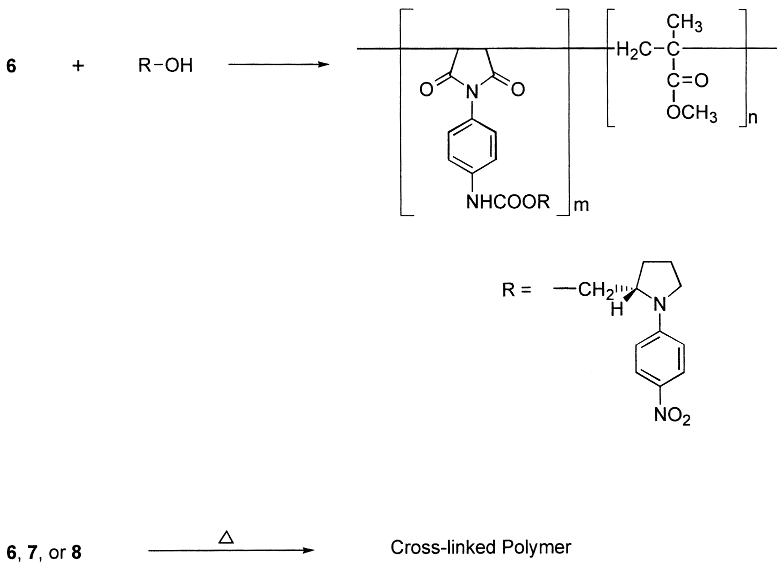
increases, indicating that the isocyanato groups were consumed through further reactions, e.g. self-crosslinking and the reaction with moisture.

Copolymerization of compound **5** with MMA was carried out in a similar manner. The polymerization results are summarized in Table 1. The copolymers were soluble in THF, DMF, and DMSO. Although the thermal reaction of the polymers was expected to generate isocyanato groups, no peak corresponding to them was observed by i.r. measurement even above 100°C. D.s.c. showed glass transitions between 145 and 180°C with the MMA copolymers of 90–50% MMA contents. Broad endothermic peaks appeared above 200°C, probably due to evaporation of phenol. No appreciable exotherm was observed below 200°C. This is attributable to the high boiling point of phenol (184°C), with which phenol remained near to an isocyanato group resulted from the thermal reaction, acting as a nucleophile to form a urethane bond again, the equilibrium existing until phenol was removed. The forward and backward reactions at the equilibrium seemed to be so fast. THA also showed evaporation of phenol above 200°C, a weight loss equivalent to phenol contents in the polymer occurring.

As mentioned above, isocyanates are very reactive and undergo a great many reactions. The coupling reaction through the formation of urethane bonds proceeded in a quantitative yield when polymer **6b** was reacted with NPP in 1,4-dioxane in the presence of DBTDL (Scheme 3). This method would be applicable to prepare the polymers having the functional substituents with poor nucleophilicity and the reactive hydrogens under the radical conditions. The coupling reaction with polymer **7** was a reaction of alcohol exchange and not as satisfactory as with polymer **6**, yielding the polymer of low contents of NPP units.

Besides the nucleophilic addition reactions with various nuclophiles self-addition of isocyanates is also known to take place. With isocyanato groups of the polymer this reaction will lead to the crosslinked structure. The reaction is believed to occur by dimerization or trimerization [3]. When heated the films prepared from polymer **6** above 140°C, the insoluble crosslinked films were obtained. The crosslinking process, however, more likely proceeded via the formation of urea bonds. Part of the isocyanato groups would be reacted first with moisture in the atmosphere to yield amino groups, which would undergo the further reaction with other isocyanato groups, resulting in the formation of urea bonds.

The crosslinked films from polymer **7** were also obtained when heated above 200°C. Fig. 3 shows TGA thermograms of polymer **7** with MMA contents of 90%. Before curing,



Scheme 3.

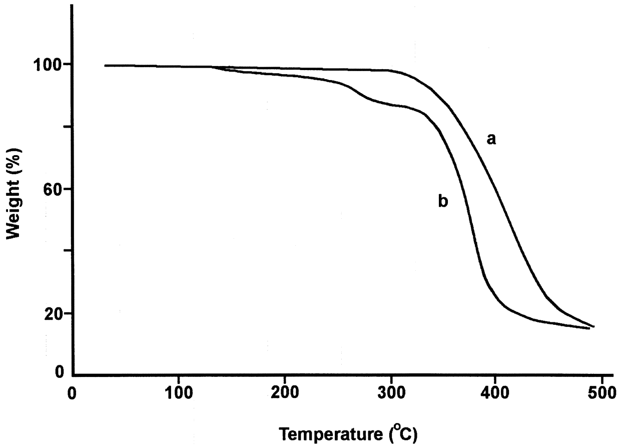


Fig. 3. TGA thermograms of polymer **7a**: (a) after curing at 200°C for 1 h; (b) before curing.

the weight loss corresponding to the evaporation of phenol occurred around 250°C. The polymer solution in THF was cast on a glass plate and cured at 200°C for 1 h to give a pale brown film. In the TGA thermogram of the film, no weight loss was observed up to 300°C. The cured film was insoluble in common organic solvents.

Compound **5** was also copolymerized with AA by initiation with AIBN (Table 1). Isocyanates are known to react with carboxylic acids to give anhydrides, which is followed by loss of carbon dioxide to eventually yield amides. Accordingly, it was expected for polymer **8** that carboxylic groups would react with isocyanato groups generated thermally from urethane units when heated. Fig. 4 shows TGA thermograms of the copolymer with AA contents of 90%. The copolymer showed about 3% weight loss up to 150°C, probably due to the evaporation of the solvents, and then was gradually degraded. After heating at 150°C for 30 min and at 220°C for an additional 30 min, its thermal stability improved dramatically, no weight loss being observed up to 300°C (Fig. 4). The cured films were pale brown and insoluble in common organic solvents. With selection of the flexible third monomers such as 2-ethylhexyl acrylate [2], this copolymerization method could be employed in preparing thermosetting acrylics for coatings.

In summary, we prepared the polymers with aromatic isocyanate precursors. On heating, isocyanato groups were generated to react with nucleophiles or under go crosslinking reaction. They are expected to have use as reactive polymers in coupling reaction with nucleophilic functional compounds or as prepolymers of thermoset polymers.

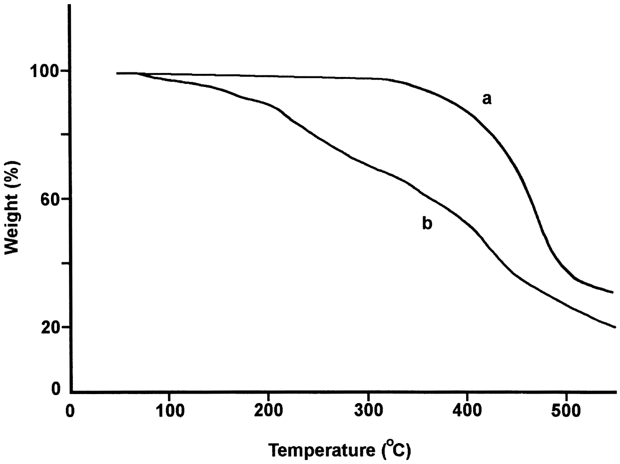


Fig. 4. TGA thermograms of polymer **8b**: (a) after curing at 250°C for 1 h; (b) before curing.

Acknowledgements

This work was supported by Korea Science and Engineering Foundation (No. 95-0502-07-01-3).

References

[1] Takemoto K, Inaki Y, Ottenbrite RM, editors. Functional monomers and polymers. New York: Marcel Dekker, 1987.
[2] Saunders KJ. Organic polymer chemistry. London: Chapman and Hall, 1988.
[3] Oertel G. Polyurethane handbook, 2nd ed. Munich: Hanser Publishers, 1994.
[4] March J. Advanced organic chemistry, 4th ed. New York: Wiley, 1992.
[5] Matsumoto A, Kubota T, Otsu T. Macromolecules 1990;23:4508.
[6] Ostu T, Matsumoto A, Kubota T, Mori S. Polym Bull 1990;23:43.
[7] Nair CPR. Macromolecules 1993;26:47.
[8] Oishi T, Fujimoto M. J Polym Sci Polym Chem Ed 1992;30:1821.
[9] Chang JY, Kim TJ, Han MJ, Choi DH, Kim N. Polymer 1997;38:4651.
[10] Hazzard BJ. Organicum. Reading, MA: Addison-Wesley, 1973. [We did not experience any explosion of compound **3** and polymer **6**. However, caution should be taken with handling azide compounds since they are known to explode very easily on rapid heating.]