

Synthesis and Characterization of Novel Polyurethanes Based on 4-((4-Hydroxyphenyl)iminomethyl)phenol

A. V. Raghu*, Han Mo Jeong*, Jae Hoon Kim, Yu Rok Lee, and Youn Bok Cho

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea

Kiran Sirsalmath

Center for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

Received July 2, 2007; Revised September 5, 2007

Abstract: Four novel polyurethanes were prepared from 4-((4-hydroxyphenyl)iminomethyl)phenol by reactions with two aromatic diisocyanates, 4,4'-diphenylmethane diisocyanate and toluene 2,4-diisocyanate, and two aliphatic diisocyanates, isophorone diisocyanate and hexamethylene diisocyanate. The polyurethanes formed were characterized by UV-vis, fluorescence, FT-IR, ¹H-NMR, ¹³C-NMR, differential scanning calorimetry, thermogravimetry, and X-ray diffraction. The polymers were semi-crystalline and all polymers were soluble in polar aprotic solvents.

Keywords: polyurethanes, Schiff base-based polymers, X-ray diffraction, thermal properties.

Introduction

Polyurethanes (PUs) have been studied in the field of polymer science because of their unique characteristics. PUs are segmented block copolymers consisting of soft segment domains derived from a polyol and hard segment domains derived from a diisocyanate and a chain extender.^{1,2} In conventional PUs, the soft segment is a polyether or polyester polyol while the hard segments contain many aromatic compounds. In literature, many types of PUs based on a number of diols and diisocyanates have been prepared and studied for various applications.³⁻¹⁰ The hard segments can also be based on polyester¹¹ or polyamide.¹² At ambient temperatures, the hard segments are incompatible with the soft segments. This induces microphase separation by crystallization or liquid-liquid demixing. The hard segment domains, dispersing in the soft matrix, act as physical junction points. Several authors¹³⁻¹⁵ have suggested that crystalline behavior and the morphology of the phase-separated PUs is quite complicated and hard segment domains have multiple transitions as a result of multifaceted morphology. Earlier, Higgins *et al.*¹⁶ carried out extensive investigations on the origin of multiple melting endotherms in hard segment of PUs using differential scanning calorimetry.

Our previous work¹⁷⁻²¹ studied Schiff base-based, azo-based, chalcone-based and hydrazide-based hard segment polyure-

thanes prepared by reactions of 2,2'-{ethane-1,2-diylbis(nitrilomethylidene)}diphenol, 2,2'-{hexane-1,6-diylbis(nitrilomethylidene)}diphenol, 2,2'-{1,4-phenylenebis(nitrilomethylidene)}diphenol, 2,2'-{4,4'-methylenedi-2-methylphenylene-1,1'-bis[nitrilomethylidene]}diphenol, 4,4'-[1,4-phenylenedi-diazene-2,1-diyl]bis(2-carboxyphenol), 4,4'-[1,4-phenylenedi-diazene-2,1-diyl]bis(2-chlorophenol), 2,6-bis(4-hydroxybenzylidene)cyclohexanone, and N¹,N²-bis[(4-hydroxyphenyl)methylene]ethanedihydrazide with different types of diisocyanates. Schiff base-based polymers have been studied for more than 50 years.²² This type of polymer contains various aromatic moieties and shows good thermal and air stability.²³⁻²⁵

Some of the polyurethanes (PUs) and polyureas were insoluble in common organic solvents due to their rigid backbones^{26,27} and were difficult to process. In an effort to prepare soluble PUs and study the hydrogen bonding in the segmented PUs, we have prepared four novel different PUs by reacting MDI, TDI, IPDI and HDI with 4-((4-hydroxyphenyl)iminomethyl)phenol. The prepared PUs were fully characterized by UV-vis, fluorescence, Fourier transform infrared (FT-IR) spectroscopy, ¹H-NMR, ¹³C-NMR, differential scanning calorimetry (DSC), thermogravimetry (TGA) and X-ray diffraction. Results are discussed in terms of their structure-morphology correlations.

Experimental

Materials. 4-Aminophenol, 4-hydroxybenzaldehyde, 4,4'-

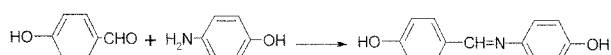
*Corresponding Authors. E-mail: hmjeong@mail.ulsan.ac.kr or gsraghu2003@yahoo.co.in

diphenylmethane diisocyanate (MDI), toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), 1,6-hexamethylene diisocyanate (HDI), and dibutyltin dilaurate (DBT) were purchased from Aldrich (Milwaukee, USA). They were used without purification. 4-Methylpentan-2-one, dimethylformamide (DMF), ethanol and methanol were purchased from Fluka.

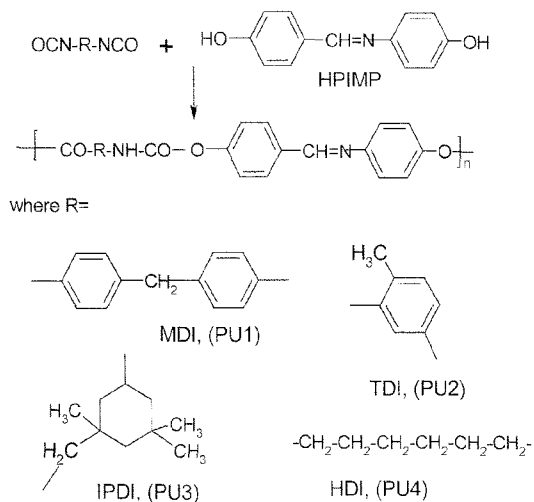
Instruments. Synthesized PUs were characterized using a UV-visible spectrophotometer (Secomam, Anthelie, France), fluorescence spectra (Varian, USA), FTIR (Varian, USA), $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ (Bruker, USA), TGA and DSC (Shelton, USA) and an X-ray diffractometer (Rigaku, Japan).

Preparation of 4-((4-hydroxyphenyl)iminomethyl)phenol [HPIMP]. To a stirred solution of 4-aminophenol (5.4 g, 0.05 mol) in hot (70 °C) ethanol (50 mL) was added dropwise a solution of 4-hydroxybenzaldehyde (12.21 g, 0.1 mol) in ethanol (75 mL). The mixture was stirred for 8 h at 70 °C. After cooling, the resultant solid precipitate was filtered, washed with ethanol and dried in air to yield 12.1 g (76%) with a m.p. of 215–218 °C. Reaction Scheme I shows the formation of HPIMP.

Synthesis of Polymers. Four kinds of PUs (PU1–PU4) were synthesized at 80 °C under nitrogen atmosphere by polyaddition of four kinds of diisocyanates with the corresponding diol HPIMP as shown in Scheme II. In a typical procedure, 0.01 mol of HPIMP was dissolved in 10 mL of dry DMF under nitrogen with one drop of dibutyltin dilaurate catalyst. The solution was stirred until the HPIMP was completely dissolved. Equal moles of diisocyanates, such as MDI, TDI, IPDI, and HDI, with respect to HPIMP were dissolved in 10 mL of dried 4-methylpentan-2-one were added once. The resulting solution was stirred continuously for 10 h



Scheme I. Reaction pathways for formation of HPIMP.



Scheme II. Reaction pathways for formation of PU1 to PU4.

at 80 °C. PUs were precipitated by pouring the reaction mixture into water and the solid was collected by filtration. Yields of PU1, PU2, PU3, and PU4 were 97%, 97%, 89%, and 96%, respectively.

Results and Discussion

Spectral Data. UV-vis and fluorescence spectra of the Schiff base-based diol and PUs were determined using DMF as a solvent at ambient temperature. Absorption spectral data of both the diol and PUs are listed in Table I. In the spectra of Schiff base-based PUs, aromatic bands around 265–276 nm are attributed to benzene $\pi-\pi^*$ transitions.²⁸ Bands around 318–326 nm are assigned to imine $\pi-\pi^*$ transitions.²⁹ Emissions from the monomer and polymers appeared around 360–380 nm and 460–490 nm, respectively. From the absorption and emission spectra, it was concluded that there was no significant difference in the monomer and the PUs prepared. The observed absorption and emission spectral data are in close agreement with our earlier report.¹⁷

FT-IR spectra of each PU shows several characteristic stretching vibrations due to the CH=N, N-H, C=O and C-H bonds as shown in Figure 1. The data were presented in Table I. The most significant feature of FT-IR of the PUs was the disappearance of isocyanate near 2300 cm^{-1} , which indicated its utilization during polymerization. Hydrogen bonding in PUs is also of great interest, since it plays an important role³⁰ in determining phase segregation. In all the PUs, broad bands appearing between 3297 and 3356 cm^{-1} were due to the presence of intermolecular hydrogen bonding between the N-H group and the carbonyl groups. However, the merged sharp bonded peak of urethane carbonyl and the imine group was shown in the region of 1655 to 1651 cm^{-1} , except in PU4. In PU4, the urethane carbonyl group appeared around 1713 cm^{-1} and the imine group appeared

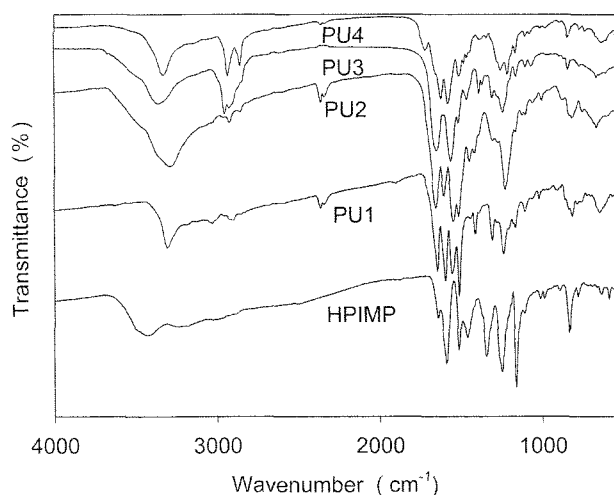


Figure 1. Representative FT-IR spectra of HPIMP and PUs (PU1 to PU4).

Table I. FT-IR, Absorption and Emission Peaks of HPIMP and PUs

Sample	FT-IR (cm ⁻¹)	Peak λ_{max} (nm)	
		Absorption	Emission
HPIMP	3423, 3025, 1631, 1588, 1463, 1346, 1245, 1162, 1004, 837	274, 319	370, 464
PU1	3360, 3030, 2905, 1651, 1596, 1546, 1404, 1229, 1163, 804	269, 325	377, 465
PU2	3297, 2922, 2856, 1655, 1596, 1537, 1446, 1230, 996, 820	265, 318	368, 475
PU3	3356, 2956, 2890, 1652, 1554, 1463, 1387, 1238, 1154, 1054, 837	272, 322	365, 482
PU4	3331, 2930, 2856, 1713, 1621, 1571, 1512, 1370, 1245, 1162, 835	276, 326	368, 471

Table II. ¹H-NMR Values of HPIMP and PUs

Sample	OH/NH Protons	Ar Protons	Methyl/Methylene/Isophorone Protons	CH = N Protons
HPIMP	10.04	6.76-7.74		8.435
PU1	9.78	6.47-8.43	3.795	8.597
PU2	9.77	6.72-8.78	2.857	8.543
PU3	9.77	6.45-7.95	0.870-3.654	8.430
PU4	9.77	6.75-8.43	1.224-3.385	8.457

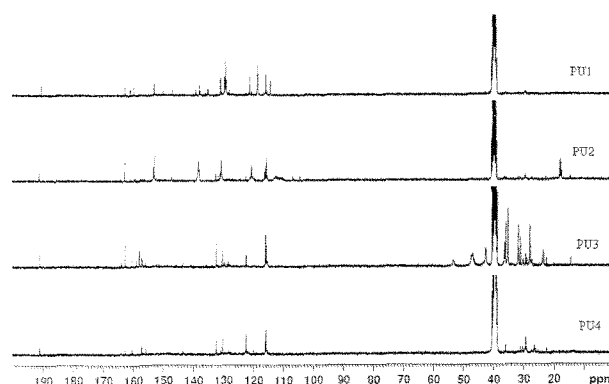
around 1621 cm⁻¹. This may be due to the presence of hexamethylene groups in the backbone.

NMR analysis shows the disappearance of -OH and -NCO groups and the formation of urethane polymer chain. ¹H-NMR spectra of PUs have shown characteristic signals and data were displayed in Table II. Resonance peaks in the region of 0.87-3.65 ppm correspond to methyl, isophorone and methylene protons of the diol as well as of the PUs. The resonance peaks of urethane protons of all the PUs observed around 9.77-9.78 ppm. The -OH proton signals of diol are observed at 10.04 ppm. The resonance peaks of imine (CH=N) protons appear in the region of 8.43-8.59 ppm. The aromatic protons occur in the region 6.45 to 8.78 ppm.

¹³C-NMR spectra of all the PUs have shown characteristic signals as shown in Figure 2, and obtained values are shown in Table III. The chemical shifts ranging between 17.79 and 53.25 are due to methyl, methylene and isophorone carbons. Resonance signals observed in the region between δ of 104.18 and 160.58 ppm are due to the aromatic carbons. Peaks observed in the region from 160.15 to 162.43 ppm are ascribed to CH=N carbons. Urethane carbonyl carbons display the signals in the region between 190.75 to 190.97 ppm.

Table III. ¹³C-NMR Values of HPIMP and PUs

Sample	Urethane Carbonyl	Ar Carbons	Methyl/Methylene/Isophorone Carbons	CH = N Carbons
HPIMP		115.62-156.99		160.15
PU1	190.75	115.23-160.58	39.23	162.36
PU2	190.97	112.20-152.93	17.79	162.43
PU3	190.94	115.65-160.15	14.02-47.06	162.39
PU4	190.90	115.65-160.16	29.04	162.34

**Figure 2.** ¹³C-NMR spectra of PUs (PU1 to PU4).

Thermal Properties. Thermal properties of all the polymers were evaluated with DSC and TGA. The derived data are shown in Tables IV and V, while the curves are displayed in Figures 3 and 4. The existence of multiple endotherms has been documented in several studies of the thermal behavior of segmented polyurethanes.³¹⁻³³ Koberstein and Galambos³⁴ indicated that the origin of multiple endo-

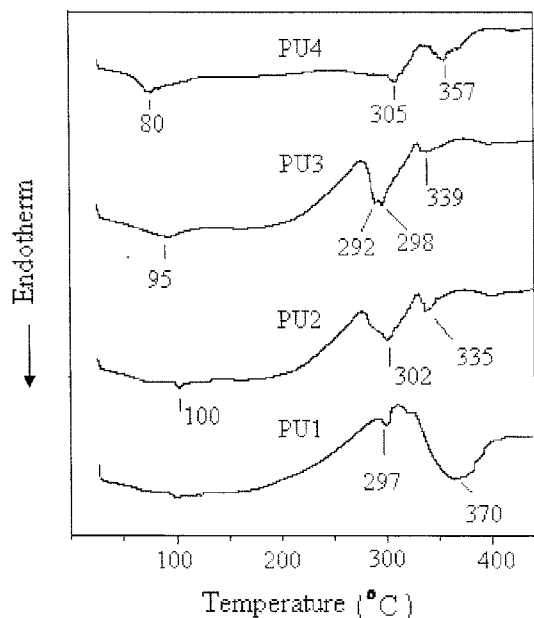


Figure 3. DSC thermograms of PU1 to PU4.

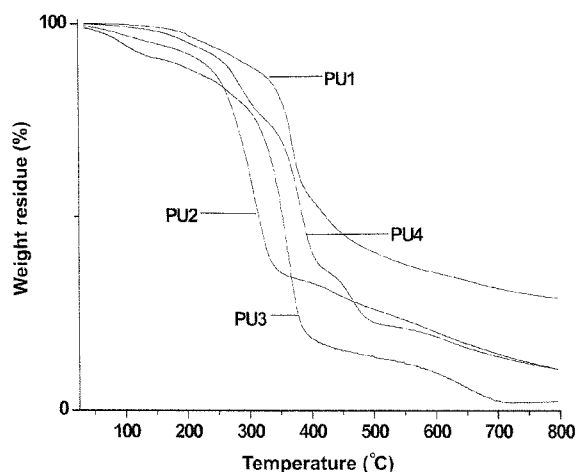


Figure 4. TGA tracings of PU1 to PU4.

therms in PUs is dependent upon the specimen preparation procedure. Martin *et al.*³⁵ suggested that the five endotherms were possibly due to melting of various hard segment length populations. The lab of van Bogart *et al.*³⁶ identified three endothermic transitions associated with the ordering of MDI/1,4-butane diol hard segments in materials subjected to a third thermal cycle. Blackwell and Lee³⁷ studied multiple melting in MDI-based PUs that had been oriented and thermally annealed. In light of the above reports, it is obvious that the melting behavior of PUs is highly dependent on the procedure adopted for sample preparation. Indeed, the origins of multiple melting may be inherently different for materials prepared under varying conditions. The existence of multiple endotherms shown in Figure 5 is in agreement with results of our previous papers.^{17-20, 26,27} DSC data of

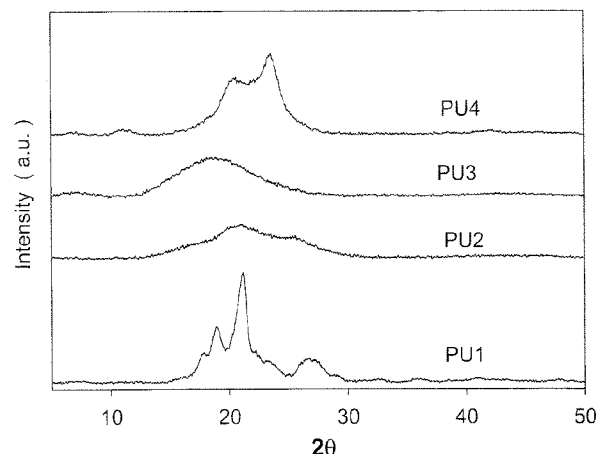


Figure 5. X-ray diffractograms of PU1 to PU4.

PU1 show two endothermic peaks, while PU2 and PU4 display three endotherms. However, PU3 exhibits four endotherms. The lowest endotherms (T_1) in the region of 80-100 °C were due to local restructuring of hard-segment units. However, intermediate temperature endotherms (T_2) were also observed at 292-305 °C which were associated with destruction of long-range orders of unspecified nature. Higher temperature endotherms (T_3) observed at 335-370 °C were generally ascribed to the melting of microcrystalline regions within the hard microdomains. MDI-based PUs displayed higher melting temperatures compared to other diisocyanate-based PUs. For all the PUs, glass transition temperatures (T_g) are not clearly shown due to alternative hard segments.³⁸

Using procedures suggested by van Krevelen,³⁹ we calculated T_g and melting temperature (T_m) values to correlate them with the experimental data as shown in Table II. Calculated T_g and T_m values fell, respectively, in the ranges of 32-106 and 241-309 °C. Due to the presence of hydrogen bonding, the T_m of hard segmented PUs were higher than that of calculated values.

Figure 4 shows the TGA thermograms. Weight loss data from TGA of all the PUs are presented in Table III. These results suggested that 10% and 50% weight losses

Table IV. Melting Endotherms from DSC

Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_g from van Krevelen ³⁴	T_m from van Krevelen ³⁴
PU1		297	370	106	309
PU2	100	302	335	95	303
PU3	95	292, 298	339	48	271
PU4	80	305	357	32	241

T_1 is the lowest temperature endotherm.

T_2 is the intermediate temperature endotherm.

T_3 is the highest melting temperature endotherm.

Table V. Thermal Properties of PUs

Sample	Decomposition Temperature (°C)		Major Weight Loss Transition (°C)	RW ₇₅₀ ^c (%)
	T ₁₀ ^a	T ₅₀ ^b		
PU1	287	426	336-462	30
PU2	229	315	252-346	12
PU3	176	352	293-391	3
PU4	252	385	272-490	12

^aTemperature at which 10% of weight loss occurred in TGA.

^bTemperature at which 50% of weight loss occurred in TGA.

^cResidual weight observed by TGA at 750 °C in N₂.

occurred in the temperature ranges of 176-287 °C and 315-426 °C, respectively. According to the curves, a major weight loss occurred between 252 °C and 490 °C, but the residual weight remaining at 750 °C ranged from 3% to 30%. TGA data indicated that MDI-based PUs exhibited better thermal stability than the other diisocyanate-based PUs. This was attributed to the presence of a biphenyl ring on the main PU chains.

X-Ray Diffraction Data. The crystalline forms of hard segments depend upon their structure as well as on crystallization conditions.⁴⁰ X-ray diffraction curves of the PUs are shown in Figure 5. PU2 and PU3 were almost amorphous in nature, but PU1 and PU4 had semi-crystalline natures. This kind of nature could be due to the symmetric structure of MDI and HDI. However, the base shift to an exothermic direction near the temperature of 250 °C in Figure 3 shows that PU2 and PU3 crystallized upon heating although it was almost amorphous when precipitated after polymerization.¹⁷

Solubility. All the PUs were soluble in polar aprotic solvents such as dimethyl acetamide, *N*-methyl-2-pyrrolidone, hexamethylphosphoramide, dimethyl sulfoxide, and dimethylformamide as well as in acidic solvents like *m*-cresol, sulphuric acid. However, they were insoluble in methylene chloride, toluene, ethanol, tetrahydrofuran, carbon tetrachloride, ethyl acetate, dioxane, ethyl methyl ketone, *n*-hexane, chloroform, and carbon disulfide.

Conclusions

Four kinds of Schiff base-based PUs, prepared by reactions of HPIMP with MDI, TDI, IPDI, and HDI, were soluble in various aprotic polar solvents and acidic solvents. However, thermal properties showed that they can hardly be processed at melt state, because their thermal degradation starts at temperatures lower than the major melting temperatures which were higher than 290 °C.

Acknowledgements. This work was supported by Brain Korea 21, Project 2007.

References

- (1) Z. Wirpsza, *Polyurethanes: Chemistry, Technology and Applications*, Ellis Horwood, London, 1993.
- (2) O. Bayer, E. Muller, S. Petersen, H. F. Piepenbrink, and E. Windemuth, *Angew. Chem.*, **62**, 57 (1950).
- (3) B. K. Kim, J. W. Seo, and H. M. Jeong, *Macromol. Res.*, **11**, 198 (2003).
- (4) P. P. G. Industries, U. K. Patent 2157702 (1985).
- (5) B. Bogdanov, V. Toncheva, E. Schacht, L. Finelli, B. Sarti, and Scandola, *Polymer*, **40**, 3171 (1999).
- (6) Y. Frere, L. Danicher, and P. Germain, *Eur. Polym. J.*, **34**, 193 (1998).
- (7) J. Y. Kwon and H. D. Kim, *Macromol. Res.*, **14**, 373 (2006).
- (8) S.-H. Kang, D.-C. Ku, J.-H. Lim, Y.-K. Yang, N.-S. Kwak, and T.-S. Hwang, *Macromol. Res.*, **13**, 212 (2005).
- (9) S. Subramani, J. M. Lee, J. H. Kim, and I. W. Cheng, *Macromol. Res.*, **13**, 418 (2005).
- (10) B. K. Kim, S. Y. Lee, and M. Xu, *Polymer*, **26**, 5781 (1996).
- (11) N. R. Legge, G. Holden, and H. E. Schroeder, *Thermoplastic Elastomers: A comprehensive review*, Carl Hansser Verlag, New York, 1987.
- (12) G. Deleens, P. Foy, and E. Marechal, *Eur. Polym. J.*, **13**, 337 (1977).
- (13) M. F. Frontini and A. Pavan, *J. Appl. Polym. Sci.*, **48**, 2003 (1993).
- (14) R. A. Phillips and S. L. Cooper, *J. Polym. Sci. Polym. Phys.*, **34**, 737 (1996).
- (15) J. T. Koberstein and A. F. Galambos, *Macromolecules*, **25**, 5618 (1992).
- (16) J. Higgins and C. S. Marvel, *J. Polym. Sci. A1*, **8**, 171 (1970).
- (17) A. V. Raghu, S. S. Jawalkar, G. S. Gadaginamath, S. B. Halligudi, and T. M. Aminabhavi, *J. Polym. Sci. Polym. Chem.*, **44**, 6032 (2006).
- (18) A. V. Raghu, G. S. Gadaginamath, N. T. Mathew, S. B. Halligudi, and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **106**, 299 (2007).
- (19) A. V. Raghu, G. S. Gadaginamath, N. T. Mathew, S. B. Halligudi, and T. M. Aminabhavi, *Reac. Funct. Polym.*, **67**, 503 (2007).
- (20) A. V. Raghu, G. Anita, Y. M. Barigaddi, G. S. Gadaginamath, and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **104**, 81 (2007).
- (21) A. V. Raghu and H. M. Jeong, *J. Appl. Polym. Sci.*, **107**, 3401 (2008).
- (22) M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).
- (23) M. Dumitriu, M. Daranga, M. Pastravanu, C. R. Dumitriu, and T. Lixandru, *Thermochimica Acta*, **134**, 177 (1988).
- (24) M. S. Patel and S. R. Patel, *J. Polym. Sci. Polym. Chem.*, **20**, 1985 (1982).
- (25) X. Li, Y. Jiao, and S. Li, *Eur. Polym. J.*, **27**, 1353 (1991).
- (26) A. V. Raghu, G. S. Gadaginamath, and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **98**, 2236 (2005).
- (27) A. V. Raghu, G. S. Gadaginamath, N. N. Mallikarjuna, and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **100**, 576 (2006).
- (28) L. Sacconi, M. Ciampolini, and Campigli, *Inorg. Chem.*, **4**, 407 (1965).
- (29) C. Mealares and A. Gandini, *Polym. Int.*, **40**, 33 (1996).

- (30) D. Evans, T. A. Hicks, W. R. N. Williamson, W. Dawson, S. C. R. Meacock, and E. A. Kitchen, *Eur. J. Med. Chem.*, **31**, 635 (1996).
- (31) R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
- (32) T. R. Hesketh, J. W. C. van Bogart, and S. L. Copper, *Polym. Eng. Sci.*, **20**, 190 (1980).
- (33) C. H. M. Jacques, *Polymer Alloys*, D. K. Klempner and K. C. Frisch, Eds., Plenum Press, New York, 1977.
- (34) J. T. Koberstein and A. F. Galambos, *Macromolecules*, **25**, 5618 (1992).
- (35) D. J. Martin, G. Meijs, P. A. Fgunatillake, S. J. McCarthy, and G. M. Renvick, *J. Appl. Polym. Sci.*, **64**, 803 (1997).
- (36) J. W. C. van Bogart, D. A. Bluemke, and S. L. Cooper, *Polymer*, **22**, 1428 (1981).
- (37) J. Blackwell and C. D. Lee, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 769 (1984).
- (38) S. Mitsuhiro, S. Masakatsu, S. Shinichi, Y. Tomoyuki, and N. Shunji, *Macromolecules*, **24**, 6254 (1991).
- (39) D. W. van Krevelen, *Properties of Polymers*, Elsevier, New York, 1990.
- (40) Z. Petrovic and J. Ferguson, *Prog. Polym. Sci.*, **16**, 695 (1991).