

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Synthesis and Characterization of Conductive Blends of Polyaniline with Poly(azomethine ester)s

L. Ravi Kumar^a; V. Sengodan^b; M. Balaji Prasad^b; K. Gopalakrishnan^b; K. Sethupathi^c

^a Department of Chemistry, C.B.M. College, Coimbatore, India ^b Department of Electronics, S.N.R. Sons College, Coimbatore, India ^c Department of Physics, Indian Institute of Technology Madras, Chennai, India

To cite this Article Kumar, L. Ravi , Sengodan, V. , Prasad, M. Balaji , Gopalakrishnan, K. and Sethupathi, K.(2007) 'Synthesis and Characterization of Conductive Blends of Polyaniline with Poly(azomethine ester)s', International Journal of Polymeric Materials, 56: 2, 197 – 206

To link to this Article: DOI: 10.1080/00914030600773628

URL: <http://dx.doi.org/10.1080/00914030600773628>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of Conductive Blends of Polyaniline with Poly(azomethine ester)s

L. Ravi Kumar

Department of Chemistry, C.B.M. College, Coimbatore, India

V. Sengodan

M. Balaji Prasad

K. Gopalakrishnan

Department of Electronics, S.N.R. Sons College, Coimbatore, India

K. Sethupathi

Department of Physics, Indian Institute of Technology Madras, Chennai, India

Polyaniline (PANI) doped with HCl was blended with different poly(azomethine ester)s (10% by weight of PANI) and compressed into pellets. The blends were studied by Fourier Transform Infra-Red (FT-IR) and thermo gravimetric analysis (TGA). Electrical conductivities of the blends determined by four-point probe method, in the temperature range 32°C to 80°C, vary from 24.4×10^{-3} to $3.15 \times 10^{-3} \text{ Scm}^{-1}$. The TGA measurements show that weight loss occurred below 80°C is only about 2%.

Keywords: blends, conductivity, polyaniline, poly(azomethine ester)s

INTRODUCTION

Polyaniline (PANI) has attracted considerable scientific interest due to its adequate level of conductivity, good environmental stability, ease of synthesis, and low cost, which makes it a potential candidate for many

Received 19 April 2006; in final form 27 April 2006.

Financial assistance for this research work in the form of minor research project by the University Grants Commission is gratefully acknowledged by the authors. They are grateful to Dr. R. Venkatesalu, The Managing Trustee of S.N.R. Sons Charitable Trust, for providing the necessary assistance to carry out this work.

Address correspondence to L. Ravi Kumar, Department of Chemistry, C.B.M. College, Coimbatore 641 042, India. E-mail: lravikumarcbm@sify.com

advanced technological applications [1]. However, poor processability of PANI hampers its commercial exploitation. Extensive research has been directed toward the improvement of the processability of PANI by copolymerization [2], doping with fictionalized protonic acids [3], and blending [4–5]. PANI blends offer several advantages such as reduced amount of PANI necessary for conductivity, increased stability of conduction, and enhanced mechanical properties of PANI [6]. Polymers that have been blended with PANI in recent times include poly(vinyl acetate) [7], polyurethane [8], polyamide [9], polyethylene [10], and nylon [11]. This article reports for the first time polyesters/co-polyesters having $-\text{CH}=\text{N}-$ chromophores in the polymer backbone as blending material for PANI. The azomethine groups are of special interest due to their syn-anti isomerism and its effect on photochromic and thermal properties [12–13]. Moreover the azopolyesters blends are expected to have liquid crystalline property. It is of interest to examine the conducting property of such polyesters/PANI blends with lower PANI content. Three different azopolyesters were blended with 10% by weight of PANI, compressed into pellets and their electrical and thermal behaviors examined.

EXPERIMENTAL

Material

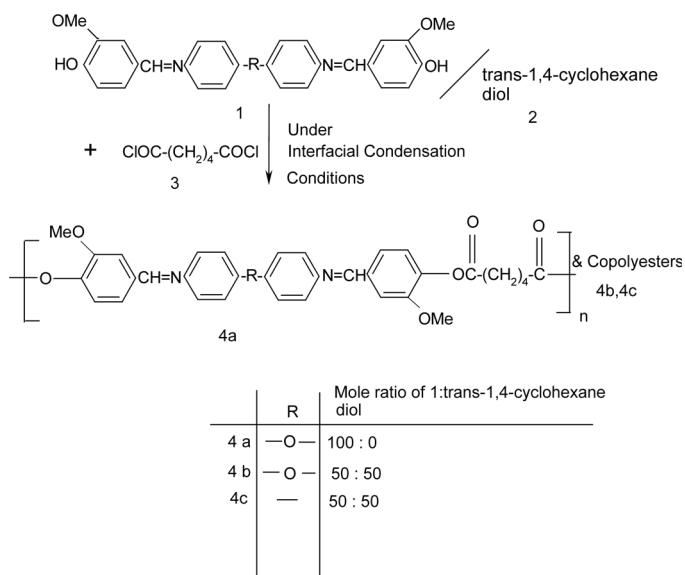
Aniline (Ranbaxy) was purified by distillation over zinc dust before use. Benzidine (Fluka), 4, 4'-diaminodiphenyl ethel (Fluka), Vanillin (Fluka) were all recrystallized from ethanol. Adipic acid (Sigma) and cyclohexanediol (Sigma) were used as received.

Polymer Synthesis

PANI was synthesized by oxidation polymerization with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. In a typical procedure, 100 ml of 0.2M aniline in aqueous H_2SO_4 at pH 1 was polymerized at 0°C by adding drop wise 100 ml of pre-cooled 0.2M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution with constant stirring. The resulting solution was, therefore, 0.1M with respect to both aniline and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. After the addition (more than 1 h), the reaction mixture was kept overnight in a refrigerator for the completion of polymerization. The settled polyaniline was filtered, washed several times with distilled water and ethanol until the washings were colorless, and finally with 0.1M HCl and the sample was dried in an oven for 6 h.

Synthesis of Azomethine Polyesters/Co-Polyesters

N, N'-Bis (4-hydroxy-3-methoxybenzylidene)-4,4'-oxydianiline (1a) and N, N'-Bis (4-hydroxy-3-methoxybenzylidene)-4,4'-benzidine (1b) were prepared by condensing vanillin with 4,4'-diamino diphenyl ether and benzidine [14]. The crude products were recrystallized from ethanol. Adipoyl chloride (3) was prepared by refluxing adipic acid with an excess of thionyl chloride. Then, the excess thionyl chloride was distilled off. The acid chloride was distilled under reduced pressure. Polyesters were synthesized through interfacial polycondensation method. In a typical procedure, monomer (1a) was stirred with aqueous sodium hydroxide in a 1:2 mole ratio under dry nitrogen at room temperature, and one equivalent of adipoyl chloride in minimum volume of freshly distilled chloroform was then quickly added. The emulsified reaction mixture was vigorously stirred for 20 min and then poured into acetone in order to coagulate the polymer. The polymer was filtered, washed with 5% Na₂CO₃ solution, dil HCl, ethanol and dried at 60°C under vacuum. In the case of co polyesters, monomers 1b or 1c and cyclohexanediol (50:50 mole ratio) were in place of monomer 1a alone. A schematic description of the polymerization is shown in Scheme 1.



SCHEME 1 Synthesis of poly (azomethine ester)s.

Preparation of PANI/Polyester Blends

PANI/polyester in weight ratio percentage of (10:90) powder was ground in a crucible for homogenous mixing. The powder was put in a hydraulic press of 5 tons load, for making the pellets. To exclude moisture, the pellets were dried in an oven at 40°C under vacuum for 6 h. The pellet sizes are 10.06 mm in diameter and thickness of 1.21 mm.

FT-IR Spectroscopic Measurements

FT-IR measurements were made on a Jasco FTIR-410 spectrophotometer with KBr pellet.

Electrical Conductivity Measurements

Conductivity measurements were carried out on a four-point probe connected to a Keithley voltmeter constant-current source system. Measurements are made by making a gentle contact at different positions of the pellet. Temperatures of the measurements were in the range 32°C to 80°C. The values obtained were completely reproducible.

TGA Measurements

The TGA data were obtained using a Universal V3.2B TA instrument in air at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Polymerization reactions of diol (1) and cyclohexanediol (2) with acid chloride (3) were carried out under interfacial conditions as reported earlier [15–16] and are represented in Scheme 1. Formation of azopolyester and copolyesters and their characterization is in line with earlier reports [15–16].

FT-IR Spectroscopic Studies

IR spectra of the blend PANI–HCl/4c powder pellet and pellet heated up to $\approx 70^\circ\text{C}$ are shown in Figure 1. For PANI–HCl (Curve A), the band at 3373 cm^{-1} is attributed to the free NH groups. The band at 3344 cm^{-1} is due to the weakly self-associated NH groups [17]. The band at 3276 cm^{-1} is in the range reported for hydrogen bonds possibly formed between the $-\text{NH}-$ and $-\text{N}=\text{CH}-$ groups [18]. On blending

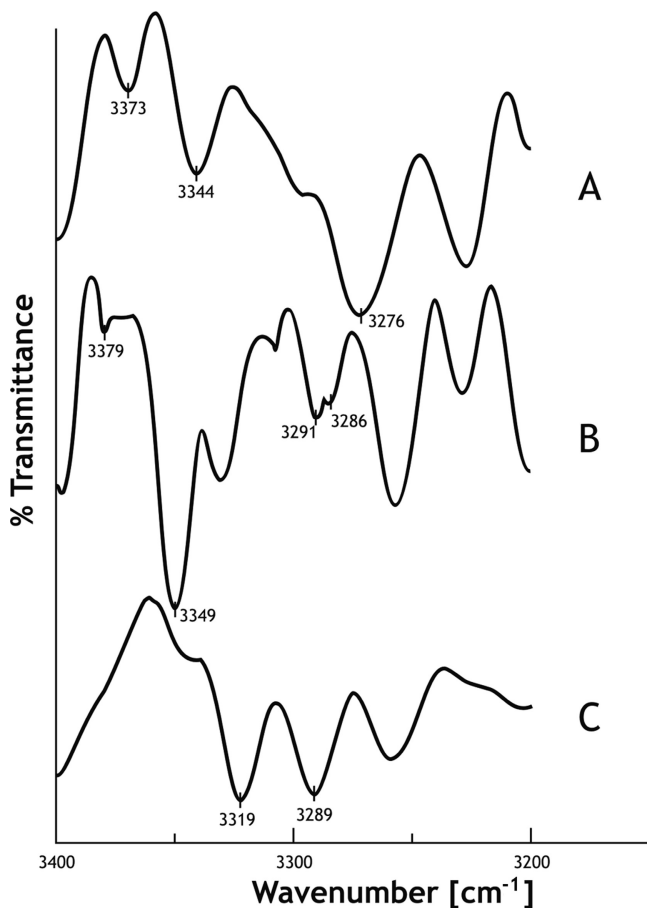


FIGURE 1 IR Spectra of PANI–HCl/polyazomethine ester blends. (Curve A: PANI–HCl; Curve B: PANI–HCl/4c powder; Curve C: PANI–HCl/4c pellet heated to $\sim 70^\circ\text{C}$).

with azopolyester 4c, in the PANI–HCl/4c powder mix (Curve B), the band at 3373 cm^{-1} is shifted to 3379 cm^{-1} and the intensity is decreased. However, the band at 3344 cm^{-1} is shifted to 3349 cm^{-1} with increased intensity. The broad band at 3276 cm^{-1} of PANI–HCl is shifted to 3291 cm^{-1} with a doublet formation. PANI–HCl/4c composite pellet after heating $\approx 70^\circ\text{C}$ (Curve C) shows a band at 3319 cm^{-1} and 3289 cm^{-1} indicating the possible interaction between NH groups of PANI/HCl and $-\text{N}=\text{CH}-$ groups of azomethine polyesters.

The quinoid $\text{C}=\text{N}$ stretching frequency and charge delocalization absorption of PANI–HCl complex and the blend PANI–HCl/4c are

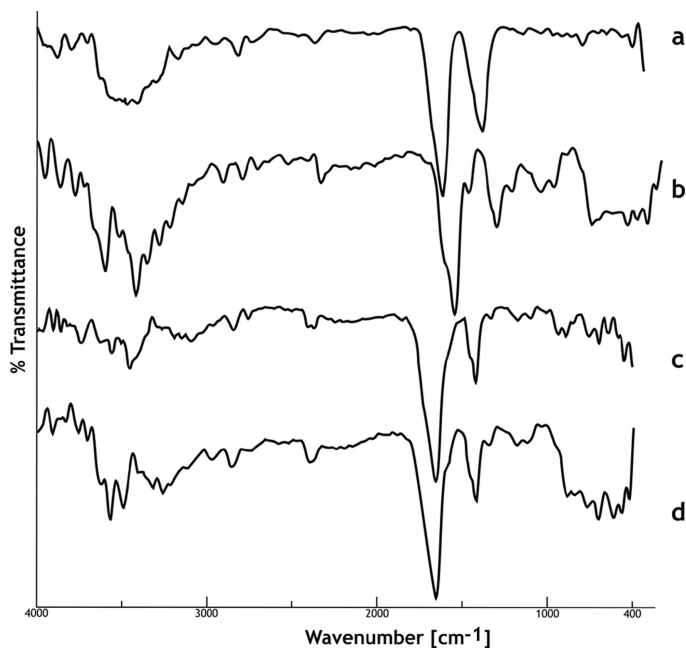


FIGURE 2 IR Spectra of PANI-HCl/polyazomethine ester blends. (Curve a: PANI-HCl; Curve b: PANI-HCl/4c powder; Curve c: PANI-HCl/4c pellet; Curve d: PANI-HCl/4c pellet heated to $\approx 70^\circ\text{C}$).

shown in Figure 2. Curve a, for PANI-HCl, shows the C=N stretching frequency at 1594 cm^{-1} and that of charge delocalization absorption [19] at 1114 cm^{-1} . The $>\text{C}=\text{N}=\text{}$ stretching frequency of the azomethine polyesters appears at 1610 cm^{-1} . Upon mixing PANI-HCl with 4c, the C=N frequency of the PANI-HCl and PANI-HCl/4c merge and were shown as doublet at 1596 cm^{-1} and 1585 cm^{-1} , respectively (Curve b). However, after making it into a pellet (Curve c) and heating to $\approx 70^\circ\text{C}$ (Curve d) the merged broad band remains almost unaltered. The charge delocalization absorption of PANI-HCl observed at 1114 cm^{-1} appeared at 1099 cm^{-1} (PANI-HCl/4c mix), 1099 cm^{-1} (PANI-HCl/4c pellet), and 1101 cm^{-1} (PANI-HCl/4c pellet heated to $\approx 70^\circ\text{C}$). These observations suggest a possible interaction of the C=N of PANI-HCl and azomethine/ester groups of the polymers. Inclusion of 10% by weight of PANI-HCl into the polymer matrix retains the charge delocalization absorption in all the examined blends suggests that the blends retain the conductivity. Similar observations were obtained for the other blends PANI-HCl/4a and PANI-HCl/4b too.

TABLE 1 Electrical Conductivity of PANI–HCl/Polyazomethine Ester Blends

Temperature ($10^3/T$) K^{-1}	PANI/4a	PANI/4b	PANI/4c
	Conductivity ($S\text{cm}^{-1}$)	Conductivity ($S\text{cm}^{-1}$)	Conductivity ($S\text{cm}^{-1}$)
3.27	5.47×10^{-3}	24.4×10^{-3}	20.5×10^{-3}
3.19	5.05×10^{-3}	18.6×10^{-3}	19.6×10^{-3}
3.09	4.54×10^{-3}	13.4×10^{-3}	18.9×10^{-3}
3.00	4.37×10^{-3}	9.44×10^{-3}	18.6×10^{-3}
2.91	4.13×10^{-3}	4.24×10^{-3}	14.8×10^{-3}
2.83	3.15×10^{-3}	3.28×10^{-3}	8.91×10^{-3}

Electrical Conductivity Studies

For the PANI–HCl blends with 4a, 4b, and 4c, the pellet size is 10.06 mm in diameter and 1.21 mm in thickness. The electrical conductivities of the blends PANI–HCl/4a, PANI–HCl/4b, and PANI–HCl/4c are given in Table 1 and Figure 3. When compared to the conductivities of 10% weight of PANI with other polymer blends [17,20] the blends reported here have a higher conductivity. This is perhaps due to the chromophoric groups that are present in the polymer backbone. As the temperature increases, the conductivity decreases (Figure 3). As the thickness of the pellet (PANI–HCl/4c*) decreases, the conductivity increases (Table 2).

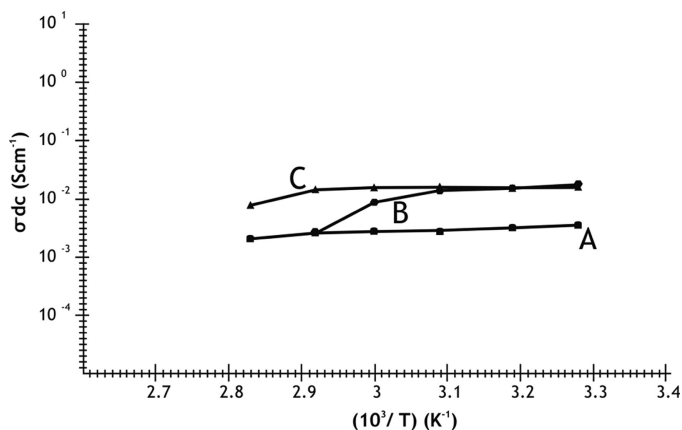


FIGURE 3 Conductivity vs. temperature variations of PANI–HCl/polyazomethine blends. (A: PANI–HCl/4a; B: PANI–HCl/4b; C: PANI–Cl/4c).

TABLE 2 Comparison of Conductivities of PANI–HCl/4c Blends for Various Pellet Dimensions

Temperature (10 ³ /T)K ⁻¹	PANI/4c*	PANI/4c ⁺
	Conductivity (Scm ⁻¹)	Conductivity (Scm ⁻¹)
3.27	20.5 × 10 ⁻³	557 × 10 ⁻³
3.19	19.6 × 10 ⁻³	251 × 10 ⁻³
3.09	18.9 × 10 ⁻³	117 × 10 ⁻³
3.00	18.6 × 10 ⁻³	90.8 × 10 ⁻³
2.91	14.8 × 10 ⁻³	82.9 × 10 ⁻³
2.83	8.91 × 10 ⁻³	38.2 × 10 ⁻³

Pellet size: * = Diameter = 10.06 mm; thickness = 1.21 mm.

⁺ = Diameter = 10.06 mm; thickness = 0.85 mm.

Thermal Stability of Blends

TG curves of the PANI–HCl/Polyester blends are shown in Figure 4. TGA data are presented in Table 3. Weight losses for the blends PANI–HCl/4a, PANI–HCl/4b, and PANI–HCl/4c at the temperature 80°C (maximum temperature at which conductivities were measured) are 2.0%, 0.9%, and 1.5%, respectively. This is attributed to the loss of volatile solvents trapped in the polymer. Thermal stability of the blend PANI/4c is higher when compared to the blends derived

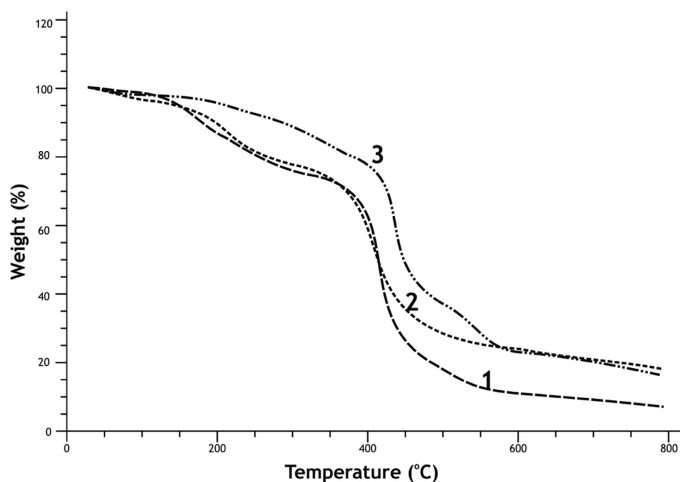
**FIGURE 4** TG curves of PANI–HCl/polyazomethine ester blends (1: PANI–HCl/4a; 2: PANI–HCl/4b; 3: PANI–HCl/4c).

TABLE 3 Thermogravimetric Analysis of PANI–HCl/ Polyazomethine Ester Blends

Blend	Temperature °C of various % decomposition		
	10%	20%	50%
PANI/4a	210	330	428
PANI/4b	190	290	417
PANI/4c	300	410	475

from azomethine polyesters 4a and 4b. This is perhaps due to the presence of benzidine rings in the stiff polymer backbone. 10% weight loss from the blends investigated starts from 210°C, 190°C, and 300°C for PANI–HCl/4a, PANI–HCl/4b, and PANI–HCl/4c, respectively.

CONCLUSIONS

PANI–HCl/Polyazomethine ester blends containing 10% weight of PANI–HCl shows electrical conductivities in the range 117×10^{-3} to $9.94 \times 10^{-3} \text{Scm}^{-1}$ depending on the type of polyazomethine ester blended. FT-IR studies show the possibility of interaction between azomethine groups of polyester with PANI–HCl. Thermal stability of the blends is in the order PANI–HCl/4c > PANI–HCl/4a > PANI–HCl/4b. Blends containing benzidine link in the polymer backbone show better conductivity and thermal stability, possibly due to their extended conjugation.

REFERENCES

- [1] Paul, E. W., Ricco, A. J., and Wrighton, M. S., *J. Phys. Chem.* **89**, 1441 (1985).
- [2] Nguyen, M. T., Kasai, P., Miller, J. L., and Diaz, A. F., *Macromolecules* **27**, 362 (1994).
- [3] Trivedi, C. D. and Dhawan, S. K., *Synth. Met.* **58**, 309 (1993).
- [4] Chen, S. A. and Lee, H. T., *Macromolecules* **28**, 2858 (1995).
- [5] Fu, Y. and Weiss, R. A., *Macromol. Chem. Phys.* **17**, 487 (1996).
- [6] Stockon, W. B. and Rubher, M. F., *Mater. Res. Soc. Sym. Proc.* **328**, 257 (1994).
- [7] Goh, S. H. Chan, H. S. O., and Ong, C. H., *Polymer* **37**, 26 (1996).
- [8] Rodrigues, P. C. and Akcelur, L., *Polymer* **44**, 6891 (2003).
- [9] Ghan, M. and Im, S. S., *Polymer* **41**, 3253 (2000).
- [10] Valenciano, C. R., Job, A. E., and Matosso, L. H. C., *Polymer* **41**, 4757 (2000).
- [11] Abraham, D., Bharathi, A., and Subramanaum, S. V., *Polymer* **37**, 5295 (1996).
- [12] Becker, R. S. and Rickey, W. F., *J. Am. Chem. Soc.* **89**, 1298 (1967).
- [13] Sek, D., *Eur. Polym. J.* **20**, 805 (1984).
- [14] Schiff, H. and Liebig, J., *Ann. Chem.* **131**, 118 (1964).
- [15] Mani, R., Rangaswamy, C., Ramarajan, K., and Ravikumar, L., *Macromol. Chem. Rapid Commun* **9**, 417 (1988).

- [16] Muthuswamy, A., Karthikeyan, S., Ramarajan, K., and Ravikumar, L., *J. Indian Chem. Soc.* **78**, 23 (2001).
- [17] Ong, C. H., Goh, S. H., and Chan, H. S. O., *J. Appl. Polym. Sci.* **65**, 391 (1997).
- [18] Furukawa, Y., Veda, F., Hyodo, Y., Harada, I., Nakajama, T., and Kawagoe, T., *Macromolecules* **21**, 1297 (1988).
- [19] Muruganandham, M. and Swaminathan, M., *Indian J. Chem.* **41A**, 1346 (2002).
- [20] Goh, S. H., Chan, H. S. O., and Ong, C. H., *J. Appl. Polym. Sci.* **68**, 1839 (1998).