

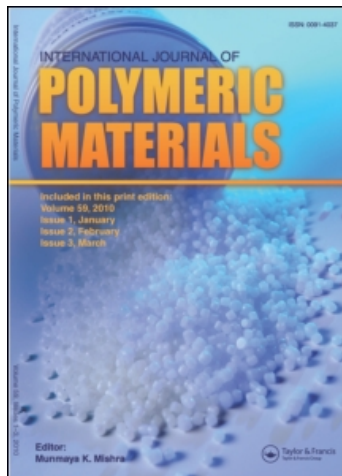
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Synthesis and Characterization of Polyamides Based on s-Triazine Moiety

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Seven polyamides containing s-triazine rings in the main chain were synthesized by high temperature polycondensation of 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-s-triazine [NANCCT] with various aromatic diamines such as 4,4'-diaminodiphenyl [DADP], 4,4'-diaminodiphenylamide [DADPA], 4,4'-diaminodiphenylsulphone [DADPS], 4,4'-diaminodiphenylsulphonamide [DADPSA], 4,4'-diaminodiphenyl methane [DADPM], 2,4-diamino toluene [DAT] and p-phenylene diamine [PPDA]. All the polyamides were characterized by solubility tests, density measurements, viscosity measurements, IR spectra, NMR spectra, and thermogravimetric analysis. The polyamides had inherent viscosities in the range 0.88–1.16 g/dL in N,N'-dimethyl formamide at room temperature (30°C). All the polyamides showed good thermal stability at high temperatures and most of them were soluble readily at room temperature in polar solvents.

Keywords: high temperature polycondensation, IR spectra, polyamides, s-triazine, thermal stability, viscosity measurements

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INTRODUCTION

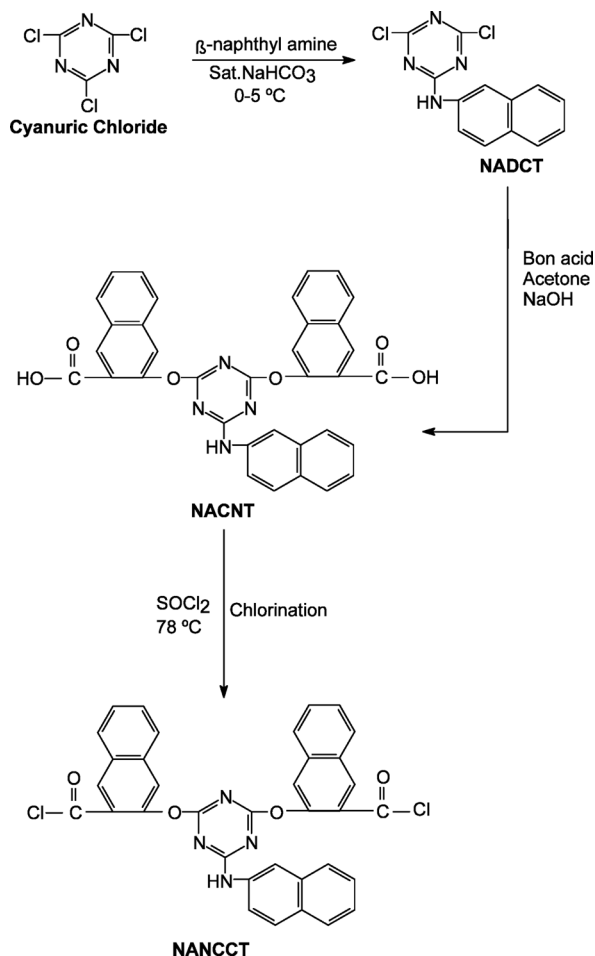
High-performance polymers are used in applications that demand service at enhanced temperatures, while maintaining their structural integrity, and an excellent combination of chemical, physical, and mechanical properties. Some of the important polymers in this respect are heterochain polymers such as polyamides, polyimides, polyethers, and so on [1–3]. Aromatic polyamides are heat resistant polymers that generally exhibit outstanding mechanical properties and excellent thermal and oxidative stability. Because of these properties they are of major commercial and industrial importance [4–5]. However, these polymers also have a common problem of being difficult to process owing to their infusibility and poor solubility in organic solvents. The reasons are strong interchain forces, inherent macromolecular rigidity, or semicrystallinity. Therefore, much effort has been made to develop structurally modified polyamides having increased solubility, in order to improve their processibility while maintaining good thermal stability. Many researchers have tackled these inherent problems over the last few decades by modifying the monomers structures [6–8], by introducing aromatic pendent groups [9–10] or heterocyclic rings [11–12] into the polyamide backbone, which impart good solubility and thermal stability.

As an approach to improve the stability and processibility of heterocyclic polymers while maintaining the thermal stability, a number of published reports have described the synthesis and properties of s-triazine ring containing polymers in the main chain, such as polyesters [13], polyamides [14], polyimides [15], polyureas [16], polyazomethines [17], and so on. It is known that polyamides containing s-triazine as a heterocyclic unit in the main chain exhibit excellent thermal stability with improved solubility [18–19]. There are many reports leading to synthesis of polyamides containing s-triazine rings in the main chain [20–23].

The present investigation involves the synthesis and characterization of new wholly aromatic polyamides using new diacid chloride monomer containing s-triazine as a heterocyclic ring, namely, 2-(β -naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-s-triazine [NANCCT] (Scheme 1) and various aromatic diamines.

MATERIALS

Dimethyl formamide, methanol, sodium hydroxide, thionyl chloride and other common chemicals used were laboratory grade reagents. Cyanuric chloride (Fluka) was purified by recrystallization from pure benzene (m.p. 146°C). β -naphthyl amine (Merck) was used as received.



SCHEME 1 Reaction Scheme for synthesis of Monomer NANCCT.

The diamines such as; 4,4'-diaminodiphenylsulphone [Cibatul, Atul (Gujarat), India], 4,4'-diaminodiphenylmethane [Cibatul, Atul (Gujarat), India], 4,4'-diaminodiphenyl (Merck), 2,4-diamino toluene (Merck), p-phenylene diamine (Merck) of purity better than 99% were used as received. Diaminodiphenylamide (DADPA) (m.p. 204°C) was synthesized by published method [24]. 4,4'-diaminodiphenylsulphonamide (DADPSA) was synthesized from acetanilide by published method [25] and purified by crystallization from alcohol and water (m.p. 137°C).

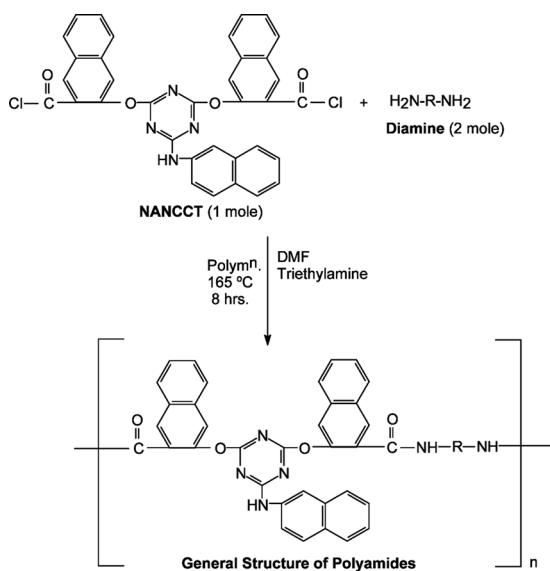
EXPERIMENTAL

Synthesis of Monomer

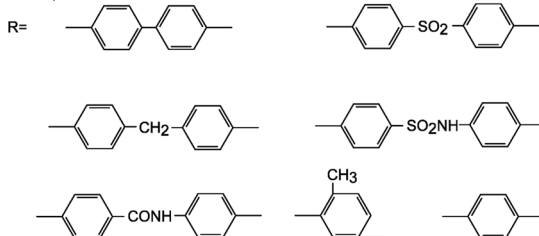
2-(β -naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-s-triazine [NANCCT] was synthesized by the reported method [26] as per reaction scheme given in Scheme 1. The yield was 90%. It was recrystallized from acetone, m.p. 200°C.

Synthesis of Polyamides

A high temperature polycondensation is exemplified in what follows for the synthesis of polyamide from 2-(β -naphthylamino)-4,6-bis-



Where,



SCHEME 2 General Reaction Scheme for synthesis for Polyamide.

(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] and diamine DADPA. General reaction scheme for the polymerization reaction for synthesizing polyamides is given in Scheme 2.

A mixture of NANCCT (5.94 g, 0.01 mol), 4,4'-diaminodiphenylamide [DADPA] (4.54 g, 0.02 mol), triethylamine (5 ml) (as an acid acceptor) and minimum quantity of DMF (approx 10 ml) was placed in a three necked flask equipped with a mechanical stirrer and drying tube. The reaction mixture was heated with stirring at 165°C for 8 h. At the initial stage of the reaction, the evolution of hydrogen chloride gas was rapid and later on it slowed down. The evolved HCl gas was absorbed by triethylamine, which is of basic nature. The polymer obtained was filtered and thoroughly washed with hot methanol and hot acetone. Finally, the polymer was dried in a vacuum oven at 80°C over night. The yield of polymer was 90%.

The other polyamides from 2-(β -naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] and various diamines such as; DADP, DADPA, DADPS, DADPSA, DADPM, DAT, and PPDA were synthesized by the similar method as shown earlier.

MEASUREMENTS

FTIR spectra of all the polyamides were recorded on Perkin Elmer FTIR Paragon 1000 SPIR S. No. 42825 using KBr pellet technique. The thermograms were obtained on a thermobalance Mettler TA-4000 system at a heating rate 10°C/min. The NMR spectra were recorded on a Perkin-Elmer Model-32 ¹H NMR spectrometer (300 MHz). Density of each polyamide was determined at 25 ± 1°C using the suspension method [27]. Reduced viscosity of polyamides was determined for 1 gm/dl solution in DMF using an Ubbelohde suspended level viscometer.

RESULTS AND DISCUSSION

The polyamides obtained from different aromatic diamines are highly soluble in polar aprotic solvents like *N*-methyl-2-pyrrolidone (NMP), *N,N'*-dimethyl formamide (DMF), *N,N'*-dimethyl acetamide (DMA) and dimethylsulphoxide (DMSO). All polyamides are a powdery substance (Table 1). The trend in viscosity reflects the relative reactivities of the diamines used.

Solubility Tests

Polyamides derived from NANCCT and various diamines are soluble in polar aprotic solvents like NMP, DMF, DMA, DMSO *m*-cresol,

TABLE 1 Physical Characteristics of Polyamides

Polyamide	Product appearance	Yield (%)	Density g/ml	n_{sp}/c (dL/g)
PADADPA	Dark brown	85	1.19	1.09
PADADPS	Dark yellow	90	1.22	0.88
PADADPSA	Light gray	90	1.21	0.92
PADADP	Dark brown	90	1.19	1.16
PADAT	Dark yellow	90	1.15	1.01
PADADPM	Yellow	90	1.16	1.12
PAPPDA	Light brown	85	1.19	0.92

and so on. The reason for this may be that the presence of bulky side groups brings about an increase in solubility [28]. It is also found that polyamides are insoluble in halogenated solvents like chloroform, carbon tetrachloride, and so on as well as in common organic solvents like acetone, methanol, benzene, cyclohexane, and so on.

Density Measurements

Density of each polyamide was determined at $25 \pm 1^\circ\text{C}$ using the suspension method. The liquid system CCl_4 and petroleum ether was found to be inert to all the polyamides. The density of the polyamides varies from 1.15 to 1.22 g/ml, as is shown in Table 1. PADADPS displays the highest density (1.22 g/ml), while PADAT shows the lowest (1.15 g/ml). This may be due to the small bond angle of SO_2 (106°), which leads to compact structure and hence the highest density value [29]. The density of polyamides varies with the different structural properties of the diamine used. The density of the polyamides decreases in the following order:



Viscosity Measurements

Dilute solution viscosity measurements were carried out using Ubbelohde suspended level kinematic viscometer. The polymer solutions were prepared in DMF and were filtered through G-3 sintered glass prior to flow time measurements. Intrinsic, reduced and inherent viscosities for all the polyamides at various concentrations were determined at $25 \pm 0.1^\circ\text{C}$. Typical Huggin's and Krammer's plots were used to obtain intrinsic viscosity for each of the polyamides. Reduced viscosity of the polyamides is shown in Table 1. Polyamide PADADPS

has the lowest (0.88 g/dL) whereas PADADP has the highest (1.16 g/dL) reduced viscosity. The trend of these values reflects the order of relative reactivity of diamines. The overall results for viscosity of polyamides reveal that all the synthesized polymers are of reasonably higher molecular weight required to possess good mechanical and thermal properties.

IR Spectral Characteristics

The IR spectrum of the polyamides exhibits several characteristic absorption frequencies (cm^{-1}). IR spectra of the polyamides are shown in Figure 1 and Figure 2.

The band observed around $3260\text{--}3350\text{ cm}^{-1}$ is attributed to N–H stretching vibration of secondary amide. The bands at $3030\text{--}3100\text{ cm}^{-1}$ are attributed to aromatic C–H stretching [30–31]. The polyamides show an absorption band in the $1640\text{--}1670\text{ cm}^{-1}$ region. This absorption, also known as amide I band, results from C=O stretching vibration. The C=O absorption occurs at lower frequency than “normal” carbonyl absorption (1715 cm^{-1}) due to resonance effect. Because the polyamides were examined in solid state, hydrogen bonding could be the major contributing

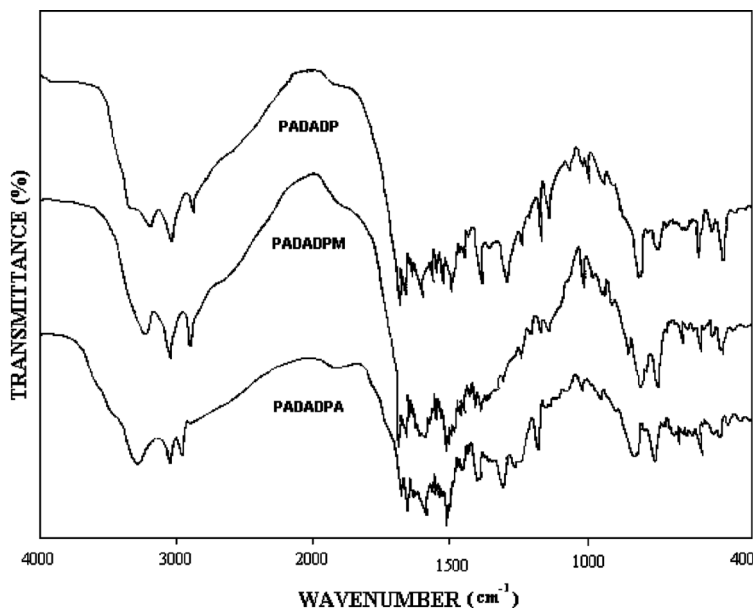


FIGURE 1 IR Spectra of polyamides.

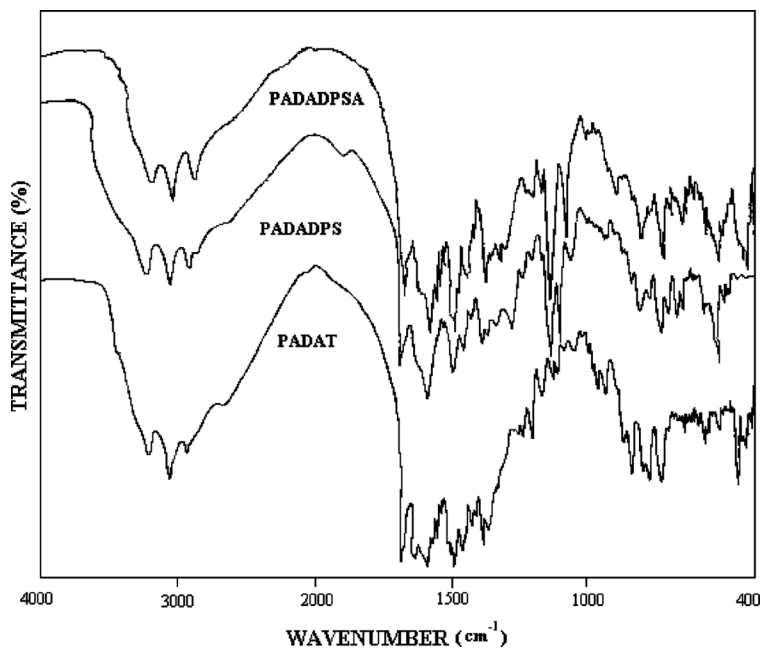


FIGURE 2 IR Spectra of polyamides.

factor to their lower carbonyl absorption. A strong amide II band that arises from the coupling of N–H bending and C=N stretching of C–N–H–H group, is located in the range 1530–1580 cm^{-1} . The strong band observed in the region 1400–1490 cm^{-1} is attributed to the skeletal and ring vibration of aromatic and heteroaromatic ring. The strong band observed around 1450–1460 cm^{-1} is due to out of plane vibration of s-triazine ring. The band in the region 1370–1425 cm^{-1} is attributed to C–N stretching vibrations of amide group. The bands at 1020 cm^{-1} and 1240–1260 cm^{-1} may be attributed to symmetric and asymmetric vibration of aryl-ether linkage.

In the IR spectra of the polyamides PADADPS, and PADADPSA, the bands observed at 1180 and 1310 cm^{-1} indicate the stretching vibration of $-\text{SO}_2$ linkage. In the spectrum of PADADPSA, a band is observed around 1370 and 1235 cm^{-1} , attributed to $-\text{SO}_2\text{NH}$ linkage. In the IR spectrum of PAPPDA a band is observed at 750 cm^{-1} that indicates the presence of four adjacent aromatic protons. The band observed at 1370 cm^{-1} in PADAT is attributed to the symmetrical bending vibration of $-\text{CH}_3$.

NMR Spectral Characteristics

High resolution (300 MHz) NMR spectra of solution of polyamides were measured in deuterated dimethylsulphoxide using TMS as an internal reference. All the spectra of the polyamides were consistent with their structure and are not shown here. As a representative, the assignments of the chemical shifts for ^1H -NMR spectrum of polyamide PADADP is given: The ^1H -NMR spectrum shows chemical shift δ at 6.60–7.90 ppm (multiplet), which may be due to the presence of aromatic protons. 1 H due to $-\text{NH}$ of amide group appears around 10.30 ppm [22].

Thermogravimetric Analysis (TGA)

Thermograms for polyamides were obtained at a scan rate of $10^\circ\text{C min}^{-1}$. Thermograms of some polyamides are shown in Figure 3. This method can broadly be classified as qualitative and semiquantitative. The relative thermal markers such as initial decomposition temperature T_0 , temperature T_{10} for 10% weight loss, temperature T_{max} for maximum rate of decomposition, temperature T_s for half volatilization, are presented in Table 2. The higher the value of T_{10} the greater the thermal stability of the polymer [32]. Comparison of T_{10} for all the polyamides synthesized indicates the following decreasing order of thermal stability:

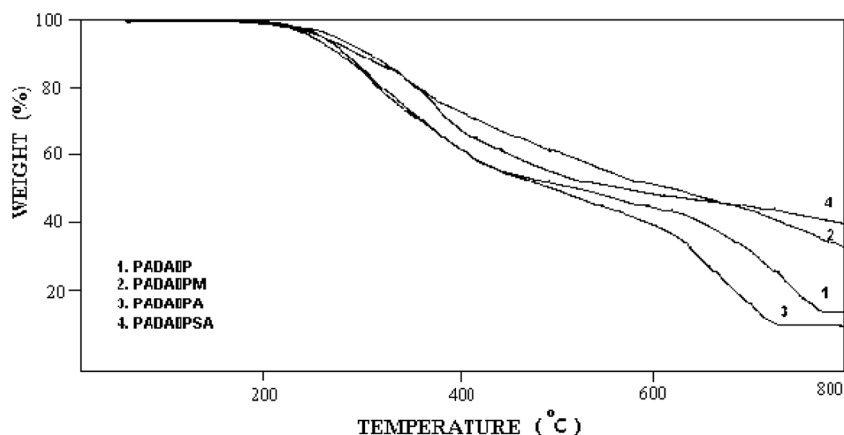
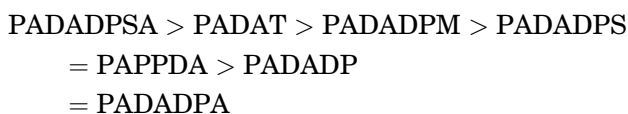


FIGURE 3 Thermograms of polyamides.

TABLE 2 Temperature Characteristics of Polyamides

Polyamide	T ₀ °C	T ₁₀ °C	T _{max} °C		T _s °C	Activation energy (KCal/mol)	
			Step-I	Step-II		Step-I	Step-II
PADADPA	250	281	383	673	523	8.16	20.97
PADADPS	237	292	372	—	549	9.94	—
PADADPSA	246	306	380	—	644	13.56	—
PADADPM	215	298	370	—	658	8.30	—
PADADP	240	281	317	740	554	12.25	—
PADAT	220	300	383	—	695	13.24	—
PAPPDA	238	292	325	710	494	13.80	14.59

A single heating rate method has been employed for the treatment of TGA data, to evaluate activation energy (E_a) for each step of thermal decomposition of polyamides. Values of activation energy [E_a] were calculated according to the methods of Broido [33]. These studies reveal that the thermal stabilities of polyamides are significantly related to the aromatic diamine component in the molecular chain. They are directly proportional to the molecular size of the diamine component.

CONCLUSION

Introduction of s-triazine rings flexibilizing linkages into the backbone of wholly aromatic polyamides results in soluble polyamides with higher thermal stability along-with good processibility. Thus, these polymers can be considered as promising, processable, high-temperature resistant high performance polymeric materials.

SYMBOLS AND ABBREVIATIONS

NADCT	2-(β -naphthylamine)-4,6-dichloro-s-triazine
NACNT	2-(β -naphthylamine)-4,6-bis(3-carboxynaphthoxy)-s-triazine
NANCCT	2-(β -naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-s-triazine
PADADPA	Polyamide of DADPA
PADADPM	Polyamide of DADPM
PADADPS	Polyamide of DADPS
PADADPSA	Polyamide of DADPSA
PADAT	Polyamide of DAT

η_{sp}/c	Reduced viscosity
T_0	Initial decomposition temperature
T_{10}	Temperature for 10% weight loss
T_{max}	Maximum rate of decomposition temperature
T_s	Temperature for 50% weight loss

REFERENCES

- [1] Ferdinand, R. (1996). *Principles of Polymer Systems*, Fourth Edition, Taylor & Francis, Washington, pp. 605–664.
- [2] Preston, J. (1988). Aromatic polyamides. In *Encyclopedia of Polymer Science Engineering*, H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., Wiley, New York, Vol. 11, pp. 381–409.
- [3] Sillion, B. (1989). Polyimides and other heteroaromatic polymers. In *Comprehensive Polymer Science*, G. Allen, Ed., Pergamon Press, Oxford, Vol. 5, pp. 499–532.
- [4] Johnson, R. N., Farnham, A. G., Hale, W. F., and Merriman, C. N., *J. Polym. Sci. Part-A: Polym. Chem.* **5**, 2375 (1967).
- [5] Jeong, H. J., Kakimoto, M., and Imai, Y., *J. Polym. Sci. Part-A: Polym. Chem.* **26**, 767 (1991).
- [6] de Abajo, J., de la Campa, J. G., Lozano, A. E., and Alvarez, J. C., *Adv. Mater.* **2**, 7 (1995).
- [7] Liaw, D. J., Liaw, B. Y., and Chen, J. J., *J. Polym. Sci. Part A: Polym. Chem.* **38**, 797 (2000).
- [8] Saegusa, Y. and Tomita, T., *Macromol. Rapid. Commun.* **5**, 21 (2000).
- [9] Kang, S. J., Hong, S. I., and Park, C. R., *J. Polym. Sci. Part A: Polym. Chem.* **3**, 936 (2000).
- [10] Suh, D. H., Ju, S. Y., Park, S. H., and Lee, J. W., *Macromol. Sci. Part A: Pure & Appl. Chem.* **38**, 751 (2001).
- [11] Banihashemi, A. and Pourabbas, B., *Eur. Polym. J.* **34**, 1809 (1998).
- [12] Tamami, B. and Yeganeh, H., *Polymer* **42**, 415 (2001).
- [13] Patel, P. M., Patel, S. K., and Patel, K. C., *Eur. Polym. J.* **36**, 861 (2000).
- [14] Yuki, Y., Sakurrai, S., Takurai, T., and Noguchi, T., *Bull. Chem. Soc. Jpn.* **43**, 2130 (1970).
- [15] Patel, H. S. and Patel, V. C., *Polymer Int.* **52**, 304 (2003).
- [16] Sarwade, B. D., Wadgaonkar, P. P., and Mahajan, S. S., *Eur. Polym. J.* **24**, 1057 (1988).
- [17] Lin, J. K., Yuki, Y., Kunisada, H., and Kondo, S., *J. Appl. Polym. Sci.* **40**, 2123 (1990).
- [18] Sarwade, B. D. and Mahajan, S. S., *J. Polym. Sci. Part-A: Polym. Chem.* **29**, 825 (1991).
- [19] Yuki, Y., Osaka, Y. and Nagoya, M., *Kogyo Daigaku Gakuho* **26**, 235 (1975).
- [20] Sagar, A. D., Salunkhe, M. M., Wadgaonkar, P. P., Sarwade, B. D., and Mahajan, S. S., *J. Polym. Sci. Part-A: Polym. Chem.* **35**, 1077 (1997).
- [21] Sagar, A. D., Shingte, R. D., Wadgaonkar, P. P., and Salunkhe, M. M., *Eur. Polym. J.* **37**, 1493 (2001).
- [22] Pal, R. R., Patil, P. S., Salunkhe, M. M., Maldar, N. N., and Wadgaonkar, P. P., *Polym. Int.* **54**, 569 (2005).
- [23] Patel, H. S. and Patel, K. C., *Iran. Polym. J.* **15**(6), 505–513 (2006).
- [24] Vogel, A. I. (1989). *Textbook of Practical Organic Chemistry*, Longman, London, pp. 1073.

- [25] Patel, K. C., Patel, N. B., and Patel, B. M., *Acta Ciencia Indica* **XXXI C(4)**, 347 (2005).
- [26] Shah, J. B., Patel, P. M., Patel, S. K., and Patel, K. C., *Ind. J. of Chem. (Sec. B)* **40B**, 734 (2001).
- [27] Weissberger, A. (1959). *Techniques of Organic Chemistry*, Third Edition, Part-1 Wiley Interscience, New York, pp. 182.
- [28] Herbenrother, P. M., *Macromolecules* **7**, 575 (1974).
- [29] Whang, W. T. and Wu, S. C., *J. Polym. Sci. Part-A: Polym Chem.* **26**, 2749 (1988).
- [30] Silverstein, R. M. (1998). In *Spectrometric Identification of Organic Compounds*, Sixth Edition, F. X. Webster, Ed., Wiley & Sons, New York, Chapter 3.
- [31] Levine, I. N. (1975). *Molecular Spectroscopy*, Wiley Interscience, New York, Chapter 6.
- [32] Koton, M. M. and Sazanov, Yu. N., *Polym. Sci. USSR* **15**, 1857 (1974).
- [33] Broido, A., *Polym. Sci. A-2* **7**, 1761 (1969).