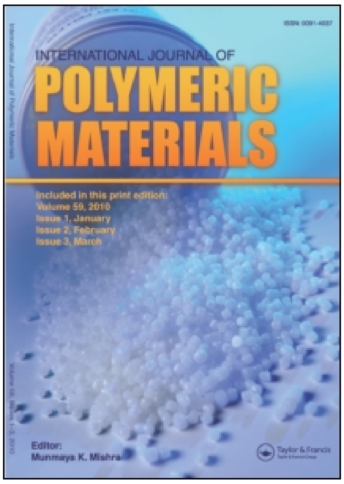

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Epoxy Modified Polyimides Part—IV

Hasmukh S. Patel[a]; Vipul J. Shah[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, India

To cite this Article Patel, Hasmukh S. and Shah, Vipul J.(1994) 'Epoxy Modified Polyimides Part—IV', International Journal of Polymeric Materials, 26: 1, 79 — 86

To link to this Article: DOI: 10.1080/00914039408029352

URL: http://dx.doi.org/10.1080/00914039408029352

Intern. J. Polymeric Mater., 1994, Vol. 26, pp. 79–86
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Printed in Malaysia

Epoxy Modified Polyimides Part—IV

HASMUKH S. PATEL* and VIPUL J. SHAH

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

(Received February 28, 1994)

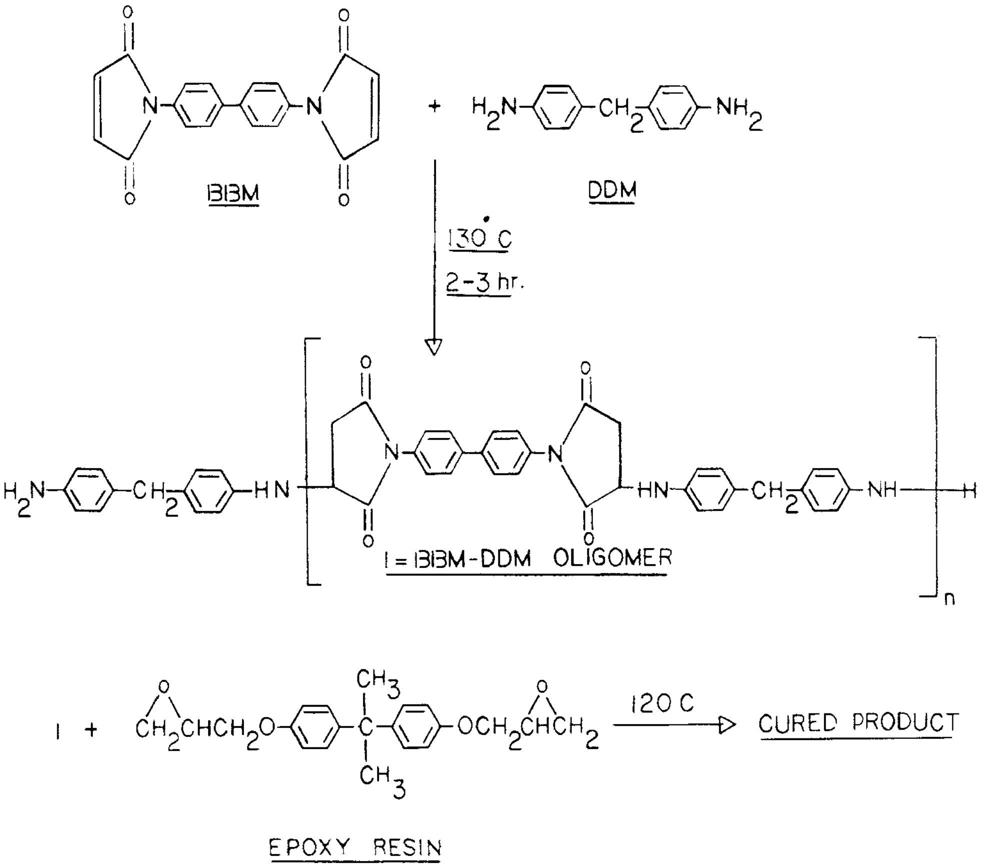
The Michael addition reaction of N,N'-benzidine bismaleimide (BBM) with 4,4'-diamino diphenyl methane (DDM) at 1:1, 1:1.5 and 1:2 molar ratios was carried out in melt at 125–130°C. The resultant oligoimides (BBM-DDM) were characterized by elemental analysis, number of amino and imino groups, IR spectral studies, number average molecular weight, by non-aqueous conductometric titration and thermogravimetry. These oligoimide were used to cure epoxy resin, namely diglycidyl ether of bisphenol-A and studied by differential scanning calorimetry (DSC). The unreinforced BBM-DDM-epoxy cured products have also been prepared and characterized.

KEY WORDS Michael addition reaction, bismaleimide, oligoimide, epoxy resin, DSC study

INTRODUCTION

Bismaleimide resin based on a Michael addition reaction of bismaleimide and diamine at higher molar ratios of bismaleimide to aromatic and aliphatic diamines are well documented as matrix resins for composites.[1–5] These resins mostly contain few amino groups and many maleimido double bonds, and these double bonds play the major role in the post curing of composite materials. The oligoimide based on bismaleimide and diamine at equimolar ratio are reported to be thermally stable materials but have less practical importance.[6–8] The area in which the reaction of epoxy resins and bismaleimide-diamine oligomers can occur (i.e., due to primary and secondary amino functionality which can exhibit epoxy curing) has received little attention either academically or industrially, in spite of well defined applications of polyimides and epoxy resins. Only a few patents[9–11] are reported in the literature in connection with epoxy resin-bismaleimide-diamine reaction technology. Such reports indicated that epoxy modified polyimide laminates have excellent heat resistance and mechanical properties. Reactions (i.e., crosslinking through the —NH_2 group) of such types of bismaleimide-diamine oligomer by the use of epoxy resin may improve the properties (especially processing and temperature performance) greatly. Hence it was decided to explore the field of epoxy modified oligoimide.

The present paper comprises the synthesis and characterization of BBM-DDM oligomers and their reaction with epoxy resin, namely diglycidyl ether of bisphenol-A (Scheme I). The BBM-DDM epoxy curing was studied kinetically by differential scanning calorimetry (DSC) as well as by curing of the unreinforced resins.



SCHEME I

RESULTS AND DISCUSSION

The objective of the work reported here was to synthesize bismaleimide-aliphatic diamine oligomers and to use these for the curing of epoxies. It was feared that the larger molecular weight bismaleimide diamine oligomer could not cure epoxy resin properly (e.g., a higher cure temperature may be needed). Hence attempts were made to establish the synthesis of BBM-DDM oligomer having lower molecular weight and more reactive amino groups.

The synthesis of BBM-DDM oligomer was performed using a slight modification of the method reported earlier.[6,8] As reported,[6,8] longer polymerizations yield high melting or softening materials. Consequently oligomerizations reported here were carried out for shorter periods. It was observed that heating of BBM at 140°C did not induce addition polymerization. This happened only at elevated temperature or by use of an initiator.[12,13] This indicated that there would be absence of poly-BBM species in the BBM-DDM oligomer. The BBM-DDMs produced are in the form of yellow powder and soften at 110–130°C depending upon the nature of the

TABLE I

Synthesis and characterization of BBM-DDM oligomers

Oligomer sample	Molar ratio of DDMBM:DDM	Yield	Elemental Analysis						Conductometric curve titration		P=Y/X	Mn[b] from first break $\left[=\frac{100}{X.10^{-3}}\right]$ (g/mol)	% wt. loss at °C from TGA				
			C		H		N		HCLO$_4$ at first break in titration curve X (meq)	HCLO$_4$ at final break in titration curve Y[a] (meq)			200	300	400	500	600
			Calc.	Found	Calc.	Found	Calc.	Found									
1	1:1	91	73.06	73.03	4.79	4.90	10.33	10.93	26.30	176	6.7	3901	4	12	31	52	86
2	1:1.5	82	72.01	72.08	4.83	5	10	10.25	42.84	180	4.2	2334	4.5	22	34	52	87.5
3	1:2	77	73	73.90	4.50	4.60	9.98	9.70	50.07	175	3.5	1997	3	17.5	30	56.5	90

[a]Considering one -NH- group in the repeating unit.

[b]$\overline{\text{Mn}} = \overline{\text{Dp}}$ X (Mol. Wt. of repeating unit).

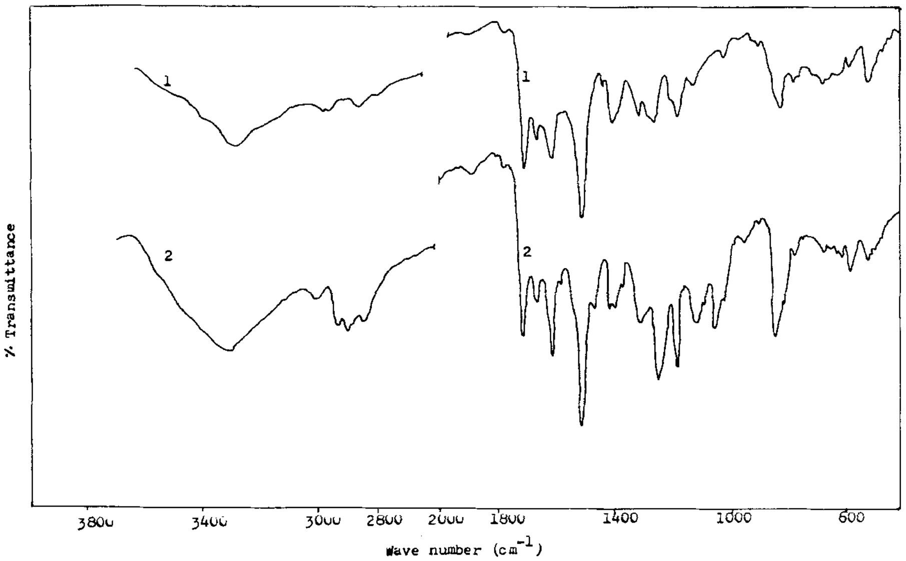


FIGURE 1 IR spectra of 1. BBM-DDM oligomer; 2. BBM-DDM oligomer with epoxy resin in the ratio 1:1.

oligomer. They are insoluble in common organic solvents. The C, H, N contents of all oligomers (Table I) are consistent with their predicted structure (Scheme I). All the three oligomers showed the red azo dye test confirming the presence of aryl amino groups. This suggests that there are terminal primary NH_2 groups in the oligomer. A typical IR spectrum of BBM-DDM is shown in Figure 1. Examination of the IR spectra of the oligomers reveals that each spectrum comprises the strong bands around 1700 cm^{-1}, 1650 cm^{-1}, 1050 cm^{-1} and 730 cm^{-1} due to the presence of the imide group.[14] The broad band around 3300 cm^{-1} is attributed to the $>$N—H bond. The inflections at 3500 cm^{-1} and 3400 cm^{-1} may arise from terminal NH_2 groups. The medium bands 2950 cm^{-1} and 2840 cm^{-1} are attributed to the C—H of the $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-$ group present in the polymer chain.[15] The absence of the band at 3010–3040 cm^{-1} (attributed to the double bond present in BBM) indicates the Michael addition polymerization of BBM and DDM. The bands observed in the fingerprint region are due to the aromatic moiety of DDM. In brief, the spectra of the BBM-DDM oligomer resemble in all aspects the spectrum reported earlier for the model compound N,N-diphenyl aspartimide.[16] The number average molecular weight of oligomers are given in Table I. The $\bar{M}n$ data show that $\bar{M}n$ values decrease with increase in molar ratio of BBM to DDM. This also indicate that the produced polymerization system yields low molecular mass oligomer rather than the high molecular mass reported earlier.[6–8] The NH and NH_2 values per repeat unit and polymer chain respectively have also been calculated on the basis of conductometric titration data.[17] These are shown in Table I. The results show that there would be more —NH_2 groups present in the oligomer prepared with a high ratio of DDM:BBM. On the basis of closeness of observed NH values and nitrogen contents of all three oligomers, the most probable structure of oligomers is that shown in Scheme I.

The TGA data of all oligomers are given in Table I. Examination of TGA data reveals that the oligomers start their decomposition around 150°C. The rate of decomposition increases between 300°C and 450°C, and oligomers decompose 90% around 600°C are shown in Figure 2.

The cure reaction of BBM-DDM epoxy was studied for two different stoichio-

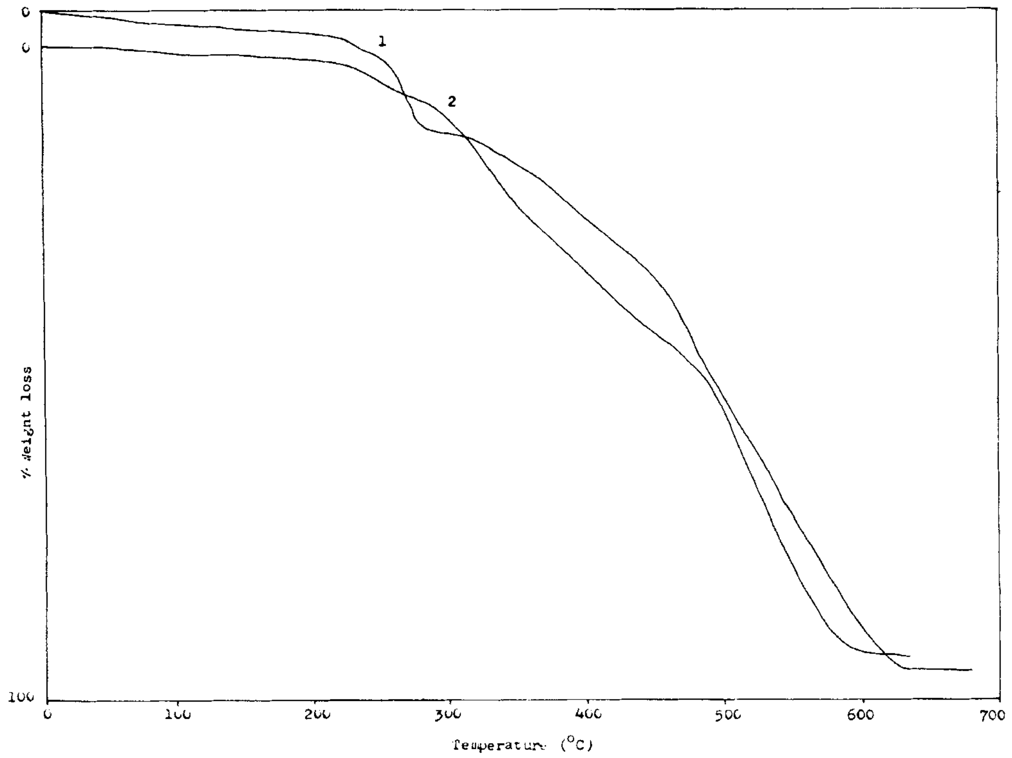


FIGURE 2 TGA of 1. BBM-DDM oligomer; 2. BBM-DDM oligomer with epoxy resin in the ratio 1:1.

TABLE II

Curing characteristic of BBM-DDM epoxy system at different heating rates

Resin System	Heating rate C/min	Oligomer epoxy ratio	Kick off Temp. Ti (°C)	Peak Temp. Tp (°C)	Final Temp. Tf (°C)	Activation energy Ea Kcal/mol	Order of Reaction
BBM:DDM (1:1)	10	1:1	108	149	173	35	0.80
		1:1.2	111.5	146	178	35.2	0.85
BBM:DDM (1:1.5)	10	1:1	116	159	186	36.80	1.25
		1:1.2	120.5	163	197	38	1.10
BBM:DDM (1:2)	10	1:1	125	167.14	197.25	40.30	1.20
		1:1.2	127	170	201.50	40.20	0.95

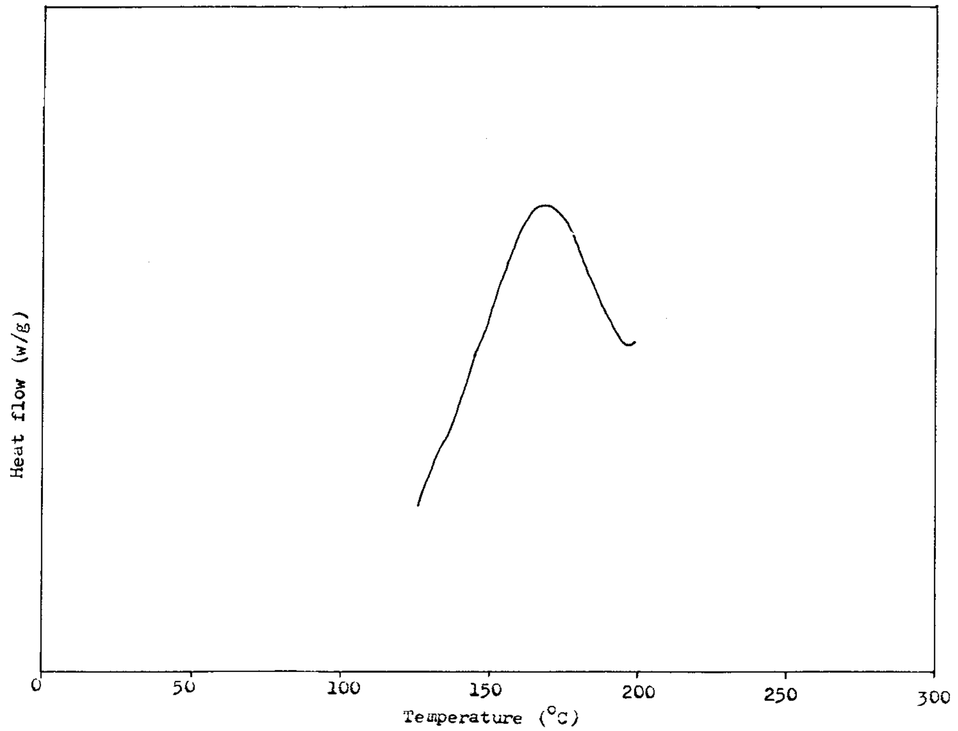


FIGURE 3 DSC curve of BBM-DDM oligomer with epoxy resin in the ratio 1:1.

metric ratios of BBM-DDM:epoxy namely 1:1 and 1:1.2 were studied. The data obtained from DSC scans are given in Table II. From the DSC thermograms obtained it was seen that all the oligoimide cured systems gave single exothermic peak in the range 108–201°C. Figure 3 shows the dynamic DSC thermogram for 10°C min^{-1}. This shows that the rate of reaction of major secondary amine and minor primary hydrogen atoms with epoxide occur simultaneously.[18] From the thermograms the kick off temperature (*Ti*), peak exotherm temperature (*Tp*) and temperature of completion of cure (*Tf*) were obtained.

The data (Table II) reveal that the curing temperature of the epoxy system increases with an increase in the molecular weight of the BBM-DDM oligomer. This behaviour is probably due to the lower rate of diffusion of the high molecular weight BBM-DDM oligomer as well as the reduced functionality, hence reactivity, compared with the lower molecular weight oligomers (see Scheme I). The values of activation energy (*Ea*) for such a system (Table II) increase with increase in the molecular weight of oligomer indicating the lower reactivity of high molecular weight oligomer. The kinetic parameters such as *E* (activation energy) and *n* (order of reaction) were calculated by assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maximum represents a point of constant convesion for each heating rate. To obtain information about the properties of unreinforced crosslinked materials, larger cured specimens were prepared using the same proportions and temperatures as stated in Table III. The unreinforced cured BBM-DDM epoxy samples are dark brown in colour and are slightly hard materials that form powder under normal pressure. They are insoluble in all common organic solvents including formic acid. They are swelled little by 25% w/v NaOH and 25% v/v HCl. Thermogravimetric analysis of all the unreinforced crosslinked materials reveals that they all degrade in a single step and start their decomposition at around 250°C. Degradation becomes faster between 475°C and 550°C. The weight loss was about 90% at 600°C in all cases.

IR spectra of three unreinforced cured products clearly show disappearances of the oxirane ring (910 cm^{-1}). The inflections at 1170 cm^{-1} in the spectra of unreinforced product obtained by using a higher proportion of epoxy may be due to the ether linkage arising from the homopolymerization of the epoxy resin by formation of tertiary amine. However, the homopolymerization of epoxy resin in only possible in the presence of tertiary amine catalyst at elevated temperature.[19]

Qualitative observations were made on glass reinforcement using a mixture of BBM-DDM epoxy resin in an organic solvent. It was noted that laminates could

TABLE III

TGA of unreinforced BBM-DDM-epoxy cured materials

Resin System	Oligomer epoxy ratio	% wt. loss at °C from TGA				
		250	300	400	500	600
BBM:DDM	1:1	2.3	5.6	26	42	88
(1:1)	1:1.2	2.1	4.9	23	40	83
BBM:DDM	1:1	4	8.4	35	57	91
(1:1.5)	1:1.2	4	8.3	32	52	89
BBM:DDM	1:1	5.2	10.5	34	56	92.6
(1:2)	1:1.2	4.8	9.3	33	58	93

be prepared with good mechanical properties (the specimen sample had impact strength of 180 mPa and flexural strength 242 mPa).

The synthesis of novel oligoimide over wide range of structure variations, their use as epoxy resin curing, the optimization of fabrication conditions and evaluation of the properties of glass reinforced composites are under progress.

EXPERIMENTAL

Materials

Diamines, namely 4,4′-diamino diphenyl methane and N,N′-benzidine were obtained from SDS Chemicals, India. The N,N′-benzidine bismaleimide was prepared by a method reported earlier.[20] Commercial epoxy (diglycidyl ether of bisphenol-A) resin was obtained from Synpol Products Pvt. Ltd., Ahmedabad, India. Specifications of epoxy resin are as follows: epoxy equivalent weight, 190–210; viscosity at 25°C, 4–10 P; density at 25°C, 1.16–1.17 g/cm^3. All other chemicals used were of laboratory grade.

Synthesis of N,N′-benzidine bismaleimide-4,4′-diamino diphenyl methane (BBM-DDM) oligomers. Synthesis of BBM-DDM was carried out by varying the molar ratios of BBM:DDM. Ratios used were 1:1, 1:1.5 and 1:2. A typical synthesis is as follows.

To a well stirred molten state of 4,4′-diamino diphenyl methane (3.96 gm, 0.02 M), N,N′-benzidine bismaleimide (3.4 gm, 0.01 M) was added gradually at 125–130°C over a period of 30 min. The resultant homogeneous viscous mass was poured immediately into a large amount of solvent ether cooled by ice. The ether was decanted and washed twice with more ether to remove unreacted DDM. The dried powder was then washed with hot DMF (20 ml) to remove unreacted BBM. The BBM-DDM oligomer was then air dried. It was yellow in colour and the yield was 90%. The details about all three oligomers are given in Table I.

Measurements

The C, H, N contents of all oligomers and their epoxy cure products were estimated using an Elemental Analyser from Carlo Erba, Italy.

The IR spectra of all oligomers and their epoxy cured products were scanned in KBr pellets on a Perkin Elmer 983 Spectrophotometer.

The number average molecular weight ($\bar{M}n$) of BBM-DDM oligomers were determined by a non aqueous conductometric titration method reported earlier.[21,22] A formic acid-acetic acid mixture† was used as the solvent and the standard perchloric acid in acetic acid was used as a titrant. A digital conductivity meter (Toshniwal, India) was used for the titration.

Curing of BBM-DDM epoxy resin was carried out by differential scanning calorimetry. A Du Pont 900 DSC was used for this study. The instrument was cali-

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†Laboratory grade formic acid to which an appropriate amount of acetic anhydride was added, which was used as solvent.

brated using standard materials of known heat of fusion. Curing was carried out using a single heating rate (10°C/min). The weight of the sample for this investigation was in the range of 4 to 5 mg and an empty cell was used as a reference.

Thermogravimetric analysis (TGA) of all oligomers and their epoxy cure products was carried out on a Du Pont thermobalance in air at a heating rate of 10°C/min.

CONCLUSIONS

(1) Reactive oligomers have been produced at three different molecular weight from the reaction of N,N'-benzidine bismaleimide (BBM) with 4,4'-diamino diphenyl methane (DDM). (2) These oligoimide were characterized by a variety of techniques. (3) The oligomers were used to cure epoxy resin (DGEBA). Reactivity parameters were calculated. Reactions were followed by IR analysis. As expected the lower molecular weight oligomers were more reactive than their higher molecular weight counterparts.

Acknowledgment

The authors are grateful to Professor M. N. Patel, Head, Department of Chemistry for providing research facilities.

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