

Synthesis and Characterization of Bisitaconimides. I

ANJALI SOLANKI, VEENA CHOUDHARY, I. K. VARMA

Center for Polymer Science and Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India

Received 27 June 2000; accepted 18 September 2001

ABSTRACT: This article describes the synthesis and characterization of bisitaconimides on the basis of 4,4'-diaminodiphenylether, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, 1,3-bis(4-aminophenoxy)benzene, and 1,4-bis(4-aminophenoxy)benzene. Isomerization of the itaconimides to citraconimides (varying in the range of 25–40%) was observed during synthesis. The curing exotherm and thermal stability of the cured resins depended on the backbone structure of itaconimides. The curing exotherm immediately followed the melting endotherms. These resins cured at lower temperatures than bismaleimides but thermal stability of cured bismaleimides was higher than bisitaconimides. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2277–2282, 2002

Key words: addition polyimides; imide resins; bisitaconimides; thermosetting resins; thermal stability

INTRODUCTION

Addition polyimides such as 5-norbornene-2,3-dicarboximide (nadimide), maleimide, or ethynyl-terminated imide resins are a leading class of thermosetting polyimides that have been extensively investigated in the past three decades. Their applications as matrix resins for advanced fiber-reinforced composites and adhesives, and in multilayer circuit boards in the electronic industry are well documented in the literature.^{1–7}

Nadimides as well as maleimide resins contain 1,2-disubstituted double bonds, which have a very low tendency to homopolymerize because of kinetic considerations. The propagation step is extremely slow due to steric interactions between the β -substituent of the propagating species and the two substituents of the incoming monomer molecule.⁸ Heating at high temperatures ($>200^\circ\text{C}$)

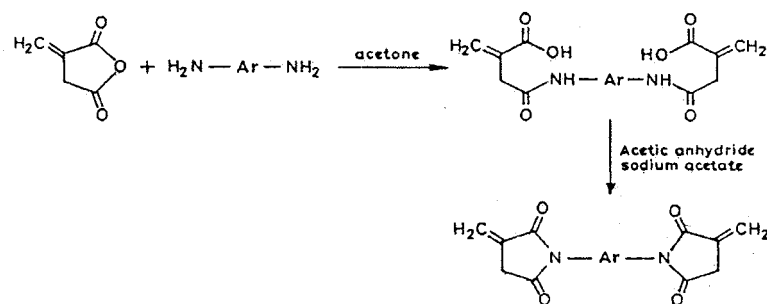
is necessary for crosslinking (curing) of bismaleimide and bisnadimide resins.

Itaconimide end-capped resins contain 1,1-disubstituted double bond, in which kinetic consideration in polymerization is of little significance. However, steric strains in the polymer, due to interactions between substituents on alternating carbon atoms, may lead to decreased ΔH values. Very few reports are available in the literature on bisitaconimides.^{9–11} It was, therefore, considered of interest to systematically study the effect of structure on curing characteristics and thermal stability of bisitaconimides and to compare their thermal characteristics with bismaleimide end-capped resins of similar structure.

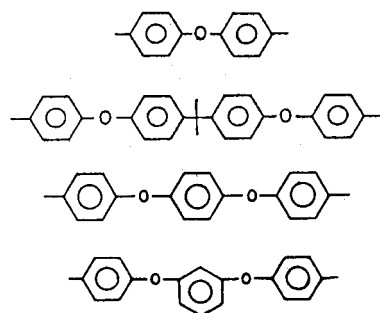
The present communication reports the thermal behavior of bisitaconimides containing ether linkages. Resins with subsequent structures were synthesized by reacting stoichiometric amounts of itaconic anhydride with appropriate diamine in acetone followed by cyclodehydration of intermediate amide acid using sodium acetate and acetic anhydride. The reaction scheme is given as:

Correspondence to: I. K. Varma.

Journal of Applied Polymer Science, Vol. 84, 2277–2282 (2002)
© 2002 Wiley Periodicals, Inc.



When Ar =



I-E

I-P

I-H

I-R

EXPERIMENTAL

Materials

Chloroform (Qualigens), phosphorus pentoxide (Merck), and 4,4'-diaminodiphenylether (Fluka) were used as received. Acetone (Qualigens) was kept over anhydrous potassium carbonate for 24 h and distilled before use. Acetic anhydride (BDH) was distilled before use and sodium acetate (Sarabhai Chemicals) was fused by heating and was stored in a desiccator. The diamines 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, 1,3-bis(4-aminophenoxy)benzene, and 1,4-bis(4-aminophenoxy)benzene were prepared in the laboratory according to the procedure reported elsewhere.¹²

Preparation of Itaconic Anhydride

Itaconic anhydride was prepared from itaconic acid by using phosphorus pentoxide (P_2O_5) as a dehydrating agent. The reaction was carried out by mixing 0.7 mol itaconic acid and 0.56 mol P_2O_5 in a 2-L reaction flask containing 750 mL chloroform. The mixture was refluxed with stirring for 24 h. After refluxing, the chloroform solution was decanted from the viscous brown residue at the bottom of the flask and the volume of this decanted solution was reduced by vacuum distillation. The solution was then cooled, resulting in crystallization of itaconic anhydride from solution. Yield = 80%, mp = 69°C.

Synthesis of Bisitaconimides

A typical procedure for synthesis of bisitaconimides is described as follows. Appropriate diamine (0.005 mol) was dissolved in 20 mL acetone in a 100-mL round-bottom flask and 0.011 mol itaconic anhydride was slowly added and the mixture was refluxed for several hours. Then, acetic anhydride and fused sodium acetate were added, and the mixture was refluxed with stirring for another 4–5 h. The bisitaconimide was precipitated in ice-cold water, washed with water, sodium bicarbonate solution, and distilled water, and dried in a vacuum oven at 50°C. Passing its solution in chloroform through silica column purified the crude imide. The chloroform solution was concentrated by distillation under reduced pressure and imide was recovered.

Characterization

Structural characterization was performed by recording IR spectra on a Bio-Rad Digilab FTS-40 FTIR spectrometer. 1H -NMR spectra were recorded on a Bruker AC 300 MHz spectrometer by using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard.

A DuPont 2100 thermal analyzer having a 910 DSC module and 951 thermogravimetric (TG) modules was used for thermal characterization. DSC scans were recorded in static air atmosphere

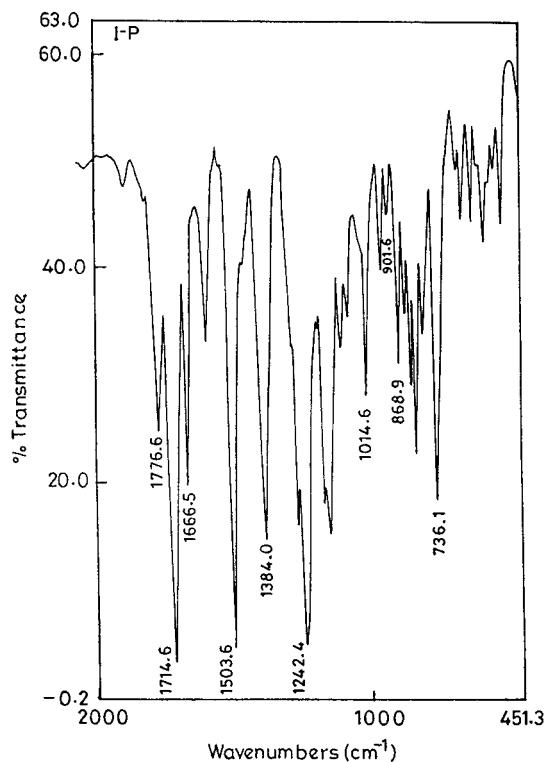


Figure 1 IR spectrum of I-P resin.

by using 7 ± 2.5 mg of sample in the temperature range of 50 – 350°C . TG studies were carried out in nitrogen atmosphere (flow rate, $60 \text{ cm}^3/\text{min}$) at a

heating rate of $10^\circ\text{C}/\text{min}$ (sample weight 10 ± 2 mg).

RESULTS AND DISCUSSION

Characterization of Bisitaconimides

Bisitaconimides were obtained in 60–70% yield. Their color ranged from light yellow (I-R, I-H) to dark yellow (I-E, I-P). These monomers were soluble in acetone, chloroform, dimethylformamide (DMF), *N,N'*dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO).

In the IR spectra of bisitaconimides (Fig. 1), the characteristic absorption bands due to imide groups were observed at 1710 ± 6 and $1770 \pm 6 \text{ cm}^{-1}$. Apart from imide bands, the $-\text{C}-\text{O}-$ stretching of the ether group was observed at $1235 \pm 10 \text{ cm}^{-1}$ and the $-\text{C}=\text{C}-$ stretch was at $1665 \pm 10 \text{ cm}^{-1}$.

In the $^1\text{H-NMR}$ spectra of bisitaconimides (Fig. 2), vinylidene protons were observed as singlets at $\delta = 5.6$ (1H) ppm and $\delta = 6.4$ (1H) ppm. The methylene protons appeared at $\delta = 3.4$ (2H, S). A complex pattern was obtained in the aromatic region, corresponding with the number of protons present in the sample. A proton resonance signal was also observed at $\delta = 2.06 \pm 0.05$ ppm. This

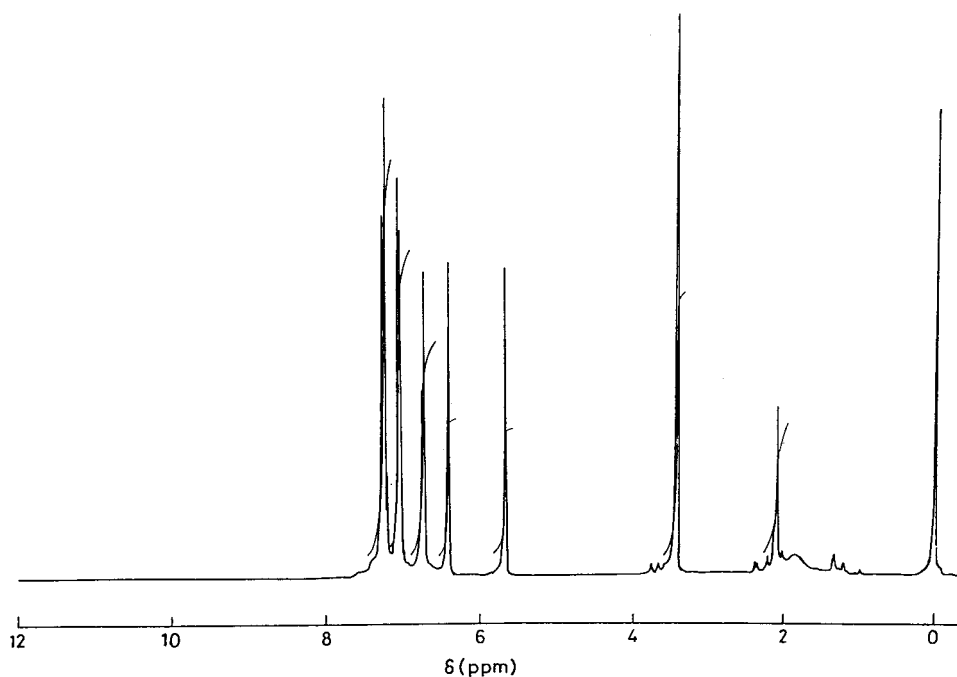


Figure 2 $^1\text{H-NMR}$ spectrum of I-R resin in CDCl_3 .

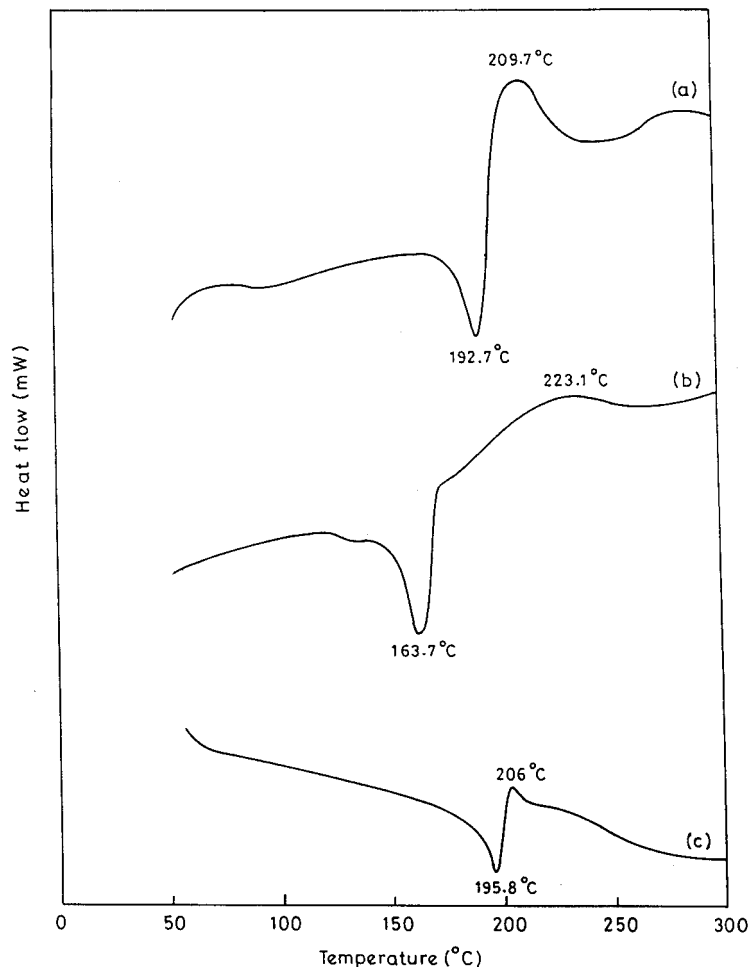


Figure 3 DSC scans of (a) I-H, (b) I-R, (c) I-E resins in static air atmosphere at a heating rate of 10°C/min.

may be attributed to the methyl group of citraconimide. The isomerization of itaconimide to citraconimide may be responsible for this signal. Such isomerization was reported earlier in itaconic anhydride.⁹ The molar fraction of citraconimide in various samples could be calculated from the ratio of protons at $\delta = 5.6$ ppm to the protons at $\delta = 2.06 \pm 0.05$ ppm and was found to be 0.25 (I-E), 0.33 (I-H), 0.36 (I-P), and 0.40 (I-R).

The DSC scans (Fig. 3) of I-E, I-R, and I-H showed sharp melting endotherms at 196, 164, and 193°C, respectively, and the curing exotherms were obtained immediately after melting. No such melting endotherm was obtained in the case of I-P and the curing exotherm was not very well defined. It is quite likely that the melting endotherm and the curing exotherm of I-P overlap each other, thereby leading to a broad ill-defined exotherm. The melting point of bismaleimides

based on 4,4'-diaminodiphenylether, 1,3-bis(4-aminophenoxy)benzene, and 1,4-bis(4-aminophenoxy)benzene was reported as 179–180,^{13,14} 174, and 233°C, respectively.¹⁵

Table I Results of DSC Studies of Bisitaconimides

| Characteristic Temperatures (°C) | Sample Designation | | |
|----------------------------------|--------------------|-----------|-----------|
| | I-E | I-R | I-H |
| T_m | 196 (180) | 164 (174) | 193 (234) |
| T_1 | 200 (219) | 182 (250) | 199 (250) |
| Texo | 206 (262) | 223 (291) | 210 (291) |
| T_2 | 211 (340) | 283 (325) | 245 (325) |
| ΔH (J/g) | – (–) | 29 (27) | 43 (66) |

Numbers in parentheses indicate the values of bismaleimides of a similar structure.

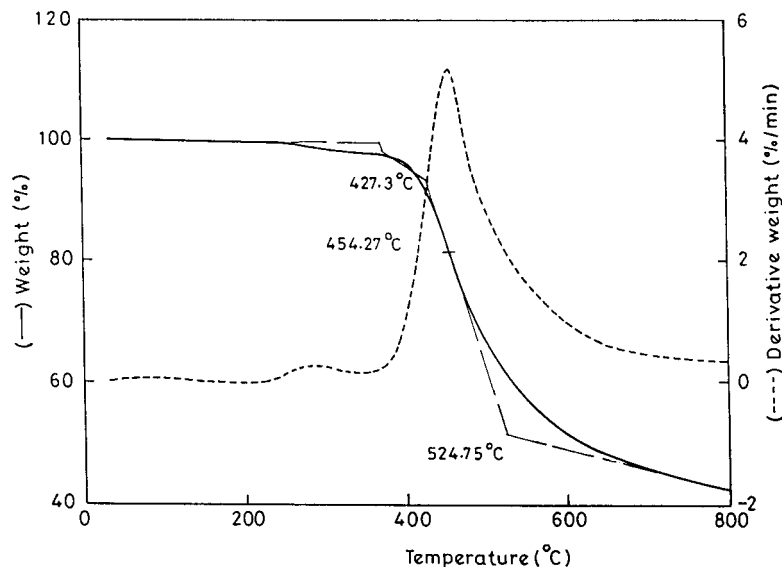


Figure 4 TG trace of I-H resin cured at 200°C for 2 h in nitrogen atmosphere at a heating rate of 10°C/min.

The curing exotherm was characterized by determining that T_1 is the kick-off temperature, where the curing starts; T_{exo} is the temperature of peak position of exotherm; and T_2 is the temperature of end of curing exotherm.

The onset temperature of curing was lowest in I-R but the exotherm was very broad, as is indicated by the difference between T_2 and T_1 . The exothermic peak temperature was in the order I-R > I-H > I-E. The curing studies of bismaleimides of corresponding structures are also given in Table I. The curing occurred at high temperature and over a broad temperature range (T_2 – T_1 results). The T_{exo} values in bismaleimide resin were higher (55–80°C) than the bisitaconimides. The heat of curing was lower in I-R than I-H resin. Similar variation in bismaleimides was observed. However, ΔH was lower in I-H than bismaleimide of similar structure.

In the TG traces (Fig. 4) of bisitaconimides, cured at 200°C for 2 h, two-step decomposition was observed for all the samples except I-P, which showed single-step decomposition. In the first step, observed in the temperature range of 200–390°C, a weight loss of 2–3% was observed. Major weight loss was observed above 300°C. To compare the thermal stability of the bisitaconimides, the TG traces were characterized by determining initial decomposition temperature (T_i), final decomposition temperature (T_f), and weight loss in this temperature range. The temperature of maximum rate of weight loss (T_{max}) was determined from differential thermogravimetric

traces (DTG). The results of these studies are summarized in Table II. On the basis of percentage char yield (Y_c) at 800°C, the following stability order was observed

$$\text{I - H} > \text{I - R} = \text{I - E} > \text{I - P}$$

Lowest char yield was obtained in I-P, which has an isopropylidene unit in the backbone, whereas

Table II Results of TG Analysis of Bisitaconimides

| Sample Designation | Decomposition Temperature (°C) | | | Wt Loss (%) | Y_c (%) |
|--------------------|--------------------------------|-------|------------------|-------------|-----------|
| | T_i | T_f | T_{max} | | |
| I-E | 250 | 391 | 323 | 3 | |
| | 391 | 682 | 482 | 58 | 39 |
| | (486) | (525) | (498) | (52) | (48) |
| I-P | 391 | 659 | 499 | 65 | 35 |
| I-R | 209 | 377 | 323 | 2 | |
| | 377 | 686 | 490 | 59 | 39 |
| | (431) | (524) | (467) | (33) | |
| | (524) | (711) | (560) | (16) | (47) |
| I-H | 204 | 345 | 282 | 2 | |
| | 345 | 709 | 454 | 56 | 42 |
| | (400) | (518) | (472) | (36) | |
| | (518) | (704) | (549) | (25) | (36) |

Numbers in parentheses indicate the values of bismaleimides of a similar structure.

the highest value was in I-H. The char yields of bismaleimides in general were higher than those of bisitaconimides.

CONCLUSION

These studies thus indicate that bisitaconimide resins having ether linkages in the backbone cure at a lower temperature than bismaleimides of similar structure. However, the thermal stability of cured bismaleimides as determined by the initial decomposition temperature and char residue at 800°C in nitrogen atmosphere was higher than bisitaconimides.

REFERENCES

1. Lin, S. C.; Pearce, E. M. *High Performance Thermosets*; Hanser: Munich, 1994; pp 13–61, 181–219, 221–246.
2. Madan, R.; Srivastava, A.; Anand, R. C.; Varma, I. K. *Prog Polym Sci* 1998, 23, 621.
3. Varma, I. K.; Sangita; Ralli, D. *Polym News* 1987, 12, 294.
4. Stenzenberger, H. D. *Br Polym J* 1988, 20, 383.
5. Loustalot, M. F. G.; Billon, L.; Sillion, B. *High Perform Polym* 1999, 11 (2), 235.
6. Delvigs, P. *High Temperature Polymer Matrix Composites*; Serafini, T. T., Ed.; Noyes Data Corp.: Park Ridge, NJ, 1987.
7. Delvigs, P.; Klopotck, D. L.; Cavans, P. J. *High Perform Polym* 1997, 9 (2), 161; 1994, 6 (3), 209.
8. Odian, G. in *Handbook of Principles of Polymerization*; Wiley: New York, 1991; pp 261–263.
9. Hartford, S. L.; Subramanian, S.; Parker, J. A. *J Polym Sci, Polym Chem Ed* 1978, 16, 137.
10. Rao, K. V. C.; Vijayan, T. M.; Bisht, M. M. S.; Nema, S. K. *Development of Bisitaconimide Resins, Polymers, and Composites, Recent Trends*; Oxford and IBH: Calcutta, 1989; p 155.
11. Solanki, A.; Choudhary, V.; Varma, I. K. *Proc. International Conference on the Thermophysical Properties of Materials*; Hing, P., Ed.; Singapore, Nov. 1999; pp 217–222.
12. Gupta, N.; Varma, I. K. *J Appl Polym Sci* 1998, 68, 1759.
13. Varma, I. K.; Sangita, Varma, D. S. *J Polym Sci, Polym Chem Ed* 1984, 22, 1419.
14. Varma, I. K.; Sangita; Gupta, S. P.; Varma, D. S. *Thermochim Acta* 1985, 93, 217.
15. Sripadraj, K.; Gupta, N.; Varma, I. K. *J Polym Mater* 1998, 15, 267; *Die Angew Makromol Chem* 1998, 260, 41.