Preparation and Characterization of Maleimide-Terminated Poly(arylene Ether Sulfone) Oligomers of Various Molecular Weights

SHIJIU JIN* and ALBERT F. YEE†

Department of Materials Science and Engineering, University of Michigan

SYNOPSIS

A new variation in the bismaleimide (BMI) resin family, maleimide-terminated poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) oligomers, has been synthesized. The preparation of oligomers (n = 1–12) is described in this study. The structure of these oligomers is characterized by FT-IR and NMR spectroscopy. These oligomers are light yellow to light gray powders that can be melted or dissolved in solvents. Their terminating group bismaleimide has relatively high reactivity. Therefore, these BMI resins can be cured at 250°C to form a crosslinked product. Since the backbone chain is poly(arylene ether sulfone), the cured polymers have high T_g's, which increased from 220°C to higher than 340°C as the number of repeating units n of the corresponding oligomers decreases.

INTRODUCTION

As aerospace technology progresses, high-performance materials are needed for many special-purpose applications. These materials need in many cases to have good thermostability, mechanical strength at high temperatures, and good retention of their properties even after a severe aging process. Unfortunately, most synthetic polymers that fit these requirements are too brittle. Therefore, the question of how best to toughen these polymers becomes very critical. Many new high-performance polymeric materials have been developed in the last two decades. The bismaleimides (BMI) prepared from diamino-diphenylene-methane is one of them[1,2] and has high T_g, high modulus, as well as thermostability once completely cured. However, the disadvantage of this BMI is that it is very brittle.

Toughening this kind of BMI by methods similar to those for epoxy resins have been attempted. These methods include mixing with liquid rubbers such as CTBN and ETBN[3-5] or by copolymerization with another oligomer to form a crosslinked copolymer with a lower crosslink density[6-11] or by preparation of BMI oligomers where the distances between two terminal reactive groups are lengthened.[12-14] For example, Kwiatkowski[12] synthesized maleimide-terminated polysulfones (BMIPS) starting from bisphenol A. With two repeat units between the end groups, the T_g of this cured resin was 185°C, which is close to that of the high T_g epoxies.

In work described in this article, we use bisphenol S instead of bisphenol A to construct maleimide-terminated poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) (Table I). These oligomers should be easy to process and cure. After being cured, they should have T_g's at least scores of degrees higher than those of BMI polysulfone prepared by Kwiatkowski and should have better thermostability.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich Chemical Co. and were used without further purification.

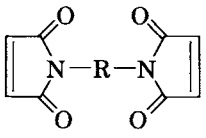
4,4-Sulfonyldiphenol	(98%, mp 245–247°C)
4-Chlorophenylsulfone	(98%, mp 145–148°C)

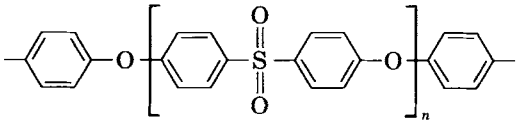
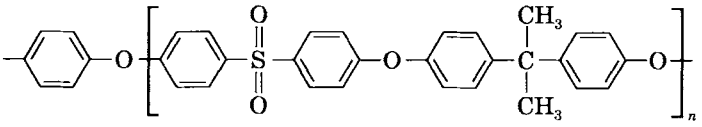
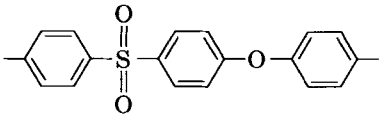
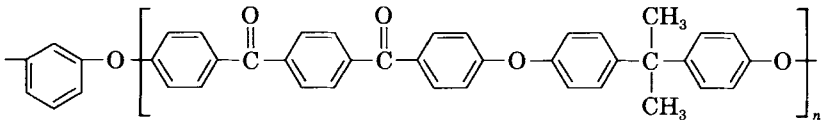
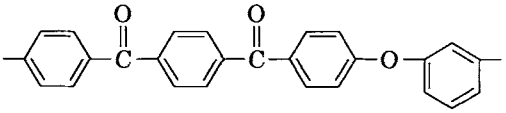
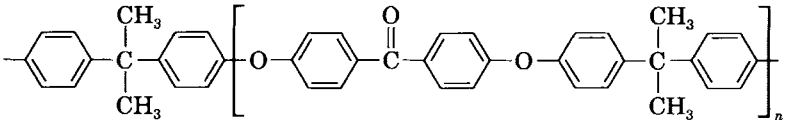
* Visiting Scientist from The Institute of Chemistry, Academia Sinica, Beijing, China.

† To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 43, 1849–1858 (1991)
 CCC 0021-8995/91/101849-10$04.00

Table I Several BMI Oligomers



Oligomer	R	Ref.
I		This work
II		
		12
III		
		13
IV		14

p-Aminophenol (98%, mp 188–190°C)

Maleic anhydride (99%, mp 54–56°C)

Oligomer Synthesis

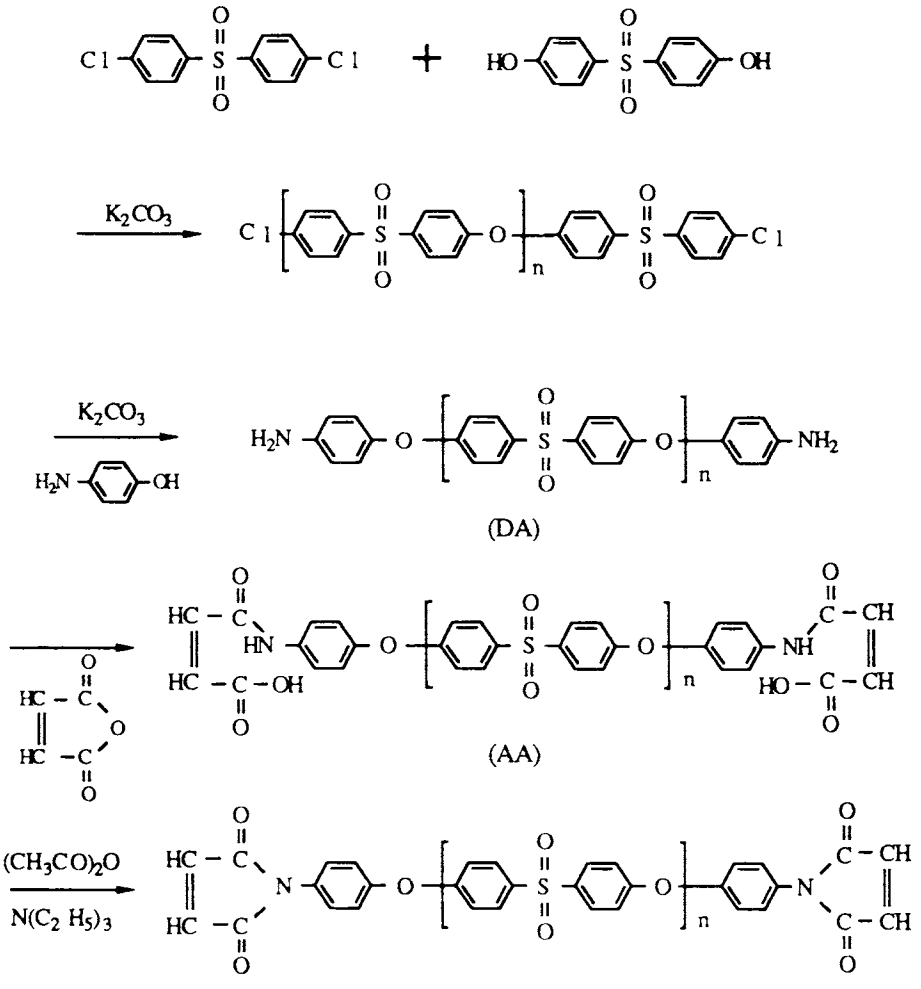
The amine-terminated poly(oxy-1,4-phenylene-1,4-sulfonyl-1,4-phenylene) oligomers (DA) of controlled molecular weight were prepared by reacting 4,4-sulfonyldiphenol, *p*-aminophenol, and 4-chlorophenylsulfone under nitrogen. The aromatic nucleophilic substitution reaction was conducted in the presence of excess potassium carbonate as the weak base, toluene as the dehydrating agent, and *N*-methylpyrrolidinone as the dipolar aprotic solvent. The dehydration reaction was for 1–2 h at 120–160°C, and the condensation polymerization was reacted at 180°C for 12 h. Then, the DA was rapidly coagulated in water. After washing with water several times, it was dried in a vacuum oven to a constant weight. The corresponding maleimide-terminated oligomers were prepared from the above DA. First, DA was reacted with maleic anhydride below 5°C in dimethylacetamide to form the amic-acid-terminated oligomers (AA). Then, by adding acetic anhydride and triethylamine, the cyclization of the amic acid was carried out immediately. The temperature of the reaction mixture was maintained at 24°C for 16–24 h and then was raised to 50°C for half an hour before stopping. The solution was poured in cold water, methanol, or their mixture. The precipitate was collected by filtration, repeatedly washed and dried at 60–70°C in a vacuum oven. The products (BMIPES) were light yellow or light gray powders and the yield was about 80%.

RESULTS AND DISCUSSION

The synthetic method of BMIPES is shown in Scheme 1. The synthesis was completed using two steps. The first step was the synthesis of the amino-terminated polysulfone (DA), and the second was the preparation of BMIPES from DA. BMIPES oligomers having different molecular weights were prepared in high yield according to our approach described here (Table II).

Polysulfones are normally synthesized by nucleophilic condensation reactions starting from bisphenol A and chloro-benzosulfone in solution.[15-17] Kwiatkowski[12] synthesized amino-terminated polysulfone oligomers starting from bisphenol A, and these oligomers were further converted to BMIPS. We synthesized similar oligomers by using bisphenol S instead of bisphenol A, but we could not use Kwiatkowski's approach simply because the nucleophilic condensation reaction was greatly influenced by the reactivity of the monomers.

Normal aromatic halides are unable to have nucleophilic substitution reactions as described earlier. The reaction will occur only when there is a strong electron withdrawing substituent (for example, $-SO_2-$, carbonyl group, etc.) in the para or ortho positions of the corresponding halides. On the other hand, the acidity of the phenol has a much greater effect on reactivity than that of halides. In aromatic nucleophilic substitution reactions, potassium phenolate is nearly 3000 times more reactive than potassium *p*-benzosulfonyl phenolate. The reactivity of potassium (*p'*-hydroxy) benzosulfonyl phenolate, however, is only 5 times greater than potassium *p*-benzosulfonylphenolate although the conjugation between phenoxyl and $-SO_2-$ groups decreases the



(DA)

(AA)

(BMIPES)

Scheme 1

Table II Molecular Weight and Product Yield of Oligomers

DA Oligomers					BMIPES Oligomers		
No.	n_{feed} (cal.)	n_p	M_n[a]	Prod. Yield (%)	No.	M_n[b]	Prod. Yield (%)
DA-07	1	1	432	93	B-7	596	92
DA-05	3	2.8	850	89	B-5	1010	97
DA-06	5	4.5	1240	93	B-6	1400	91
DA-08	7	6.8	1770	94	B-8	1934	
DA-09	11	8.9	2280	98	B-9	2440	
DA-12	15	10.3		98			
DA-10	17	12.1	3000	100			

[a] From NMR data.
[b] Cal. from M_n of the DAs.

electron withdrawing effect of the sulfonyl group. Therefore, bisphenol S has much lower reactivity compared to bisphenol A.[15] The polysulfone oligomers can be easily obtained by the reaction of sodium bisphenolate A with bischlorobisbenzoylsulfone in dimethylsulfoxide at 160°C within 1 h. But it is difficult to get good results if one uses bisphenol S to prepare polysulfone by the same method. This is true even if the reaction time was prolonged to 10 h.[16] It should be noted that the low molecular weight oligomers are difficult to precipitate. An alternative way to accelerate the reaction was to increase the reaction temperature. Unfortunately part of the dimethylsulfoxide (DMSO) started to decompose as temperature neared its boiling point (189°C). So other high boiling point solvents such as *N*-methyl-2-pyrrolidinone, tetramethyl sulfone[18] and phenylsulfone[19] must be used. We chose *N*-methyl-2-pyrrolidinone as the solvent due to several advantages. One is lower cost compared with other high boiling point solvents; another is that it is easier to be recovered and is less toxic. Another problem is the difficulty of ridding phenol of water. The existence of water will lead to the hydrolysis of phenolate and halides as well. By using solid potassium carbonate instead of an aqueous alkali solution, we can minimize the amount of water, thereby restraining the hydrolysis of phenolate. Experimental results show that our approach is successful.[20]

The ^{1}H-NMR spectra of the DAs are shown in Figure 1. The spectra show that the products conform to what we expected. The chemical shift of hydroxy-terminated and chloro-terminated polysulfone are at 7.6 and 7.7 ppm, respectively. These peaks are difficult to see in the spectra of the DAs. This means that the condensation reaction is quite complete. The peak at 5.3 ppm is due to the resonance of aromatic amino protons. Three equal intensity doublets, which appear at 6.62, 6.82, and 7.0 ppm, are assigned to the resonance of protons related to the terminal amino aromatic ring, and the resonance peak, which appears at 7.25 ppm, is assigned to the resonance of ortho protons in phenolether rings. Therefore, we can calculate the number of repeat units of oligomers, n, and its number-average molecular weight, M_n, by the integral of the NMR spetrum:

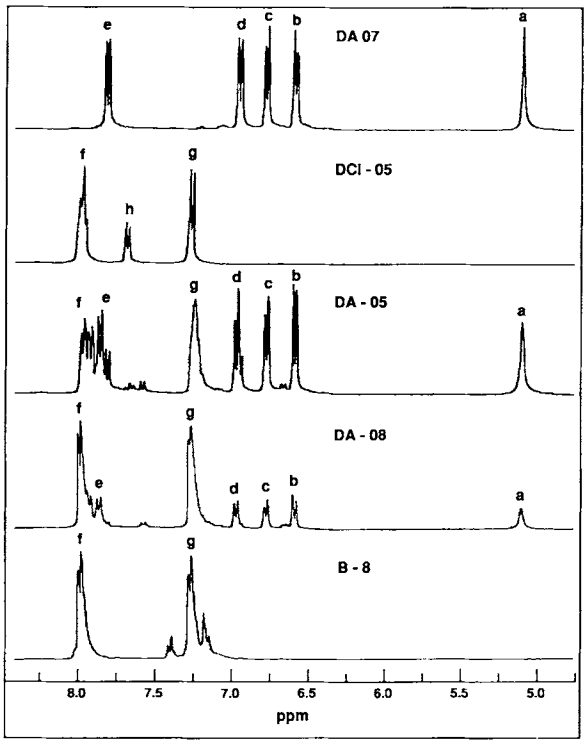
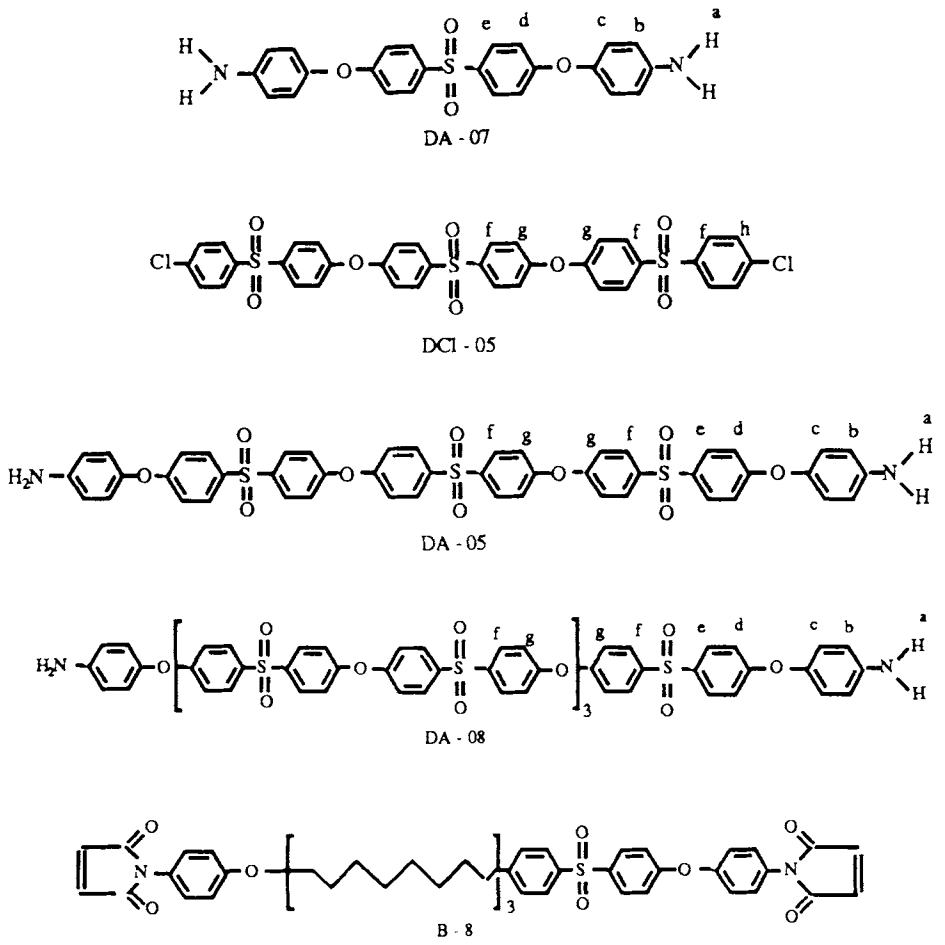


Figure 1 NMR of products (see Scheme 2).



Scheme 2

$$n = b + c + d3g$$

$$M_n = 200 + 232n$$

Where c, b, d and g are the integral areas of the corresponding NMR peaks in Figure 1, respectively.

The M_n of each DA oligomer is shown in Table II and Figure 2. They are lower than expected. This can be explained by the presence of impurities in the monomers and by side reactions.

The FT-IR spectra of the DA oligomers are shown in Figure 3. The resonance bond at about 1150 cm^{-1} is due to the vibration of the $-SO_2-$ group. The two resonance peaks at 1487 and 1505 cm^{-1} are due to the resonance of the backbone and terminal amino benzene rings, respectively. Therefore, the relative intensity of both peaks changes with the molecular weight of the oligomers. If we choose the transmittance at 1850 cm^{-1} as the base line, and plot the relative peak intensity versus M_n obtained from NMR data, a linear relationship is obtained (Fig. 4). As a result, we can also determine the molecular weight of the DA oligomer in terms of the IR data.

The transformation of maleic anhydride and

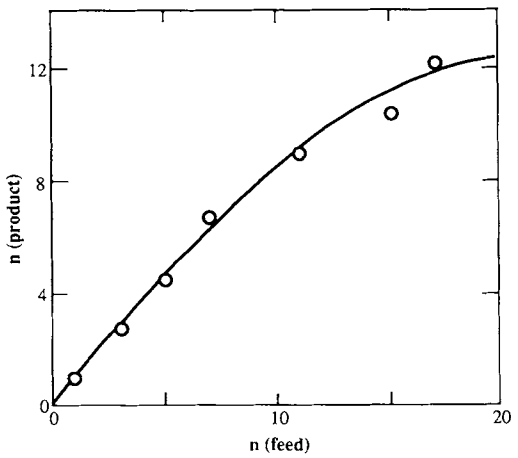


Figure 2 Relation between n (feed) and n (product).

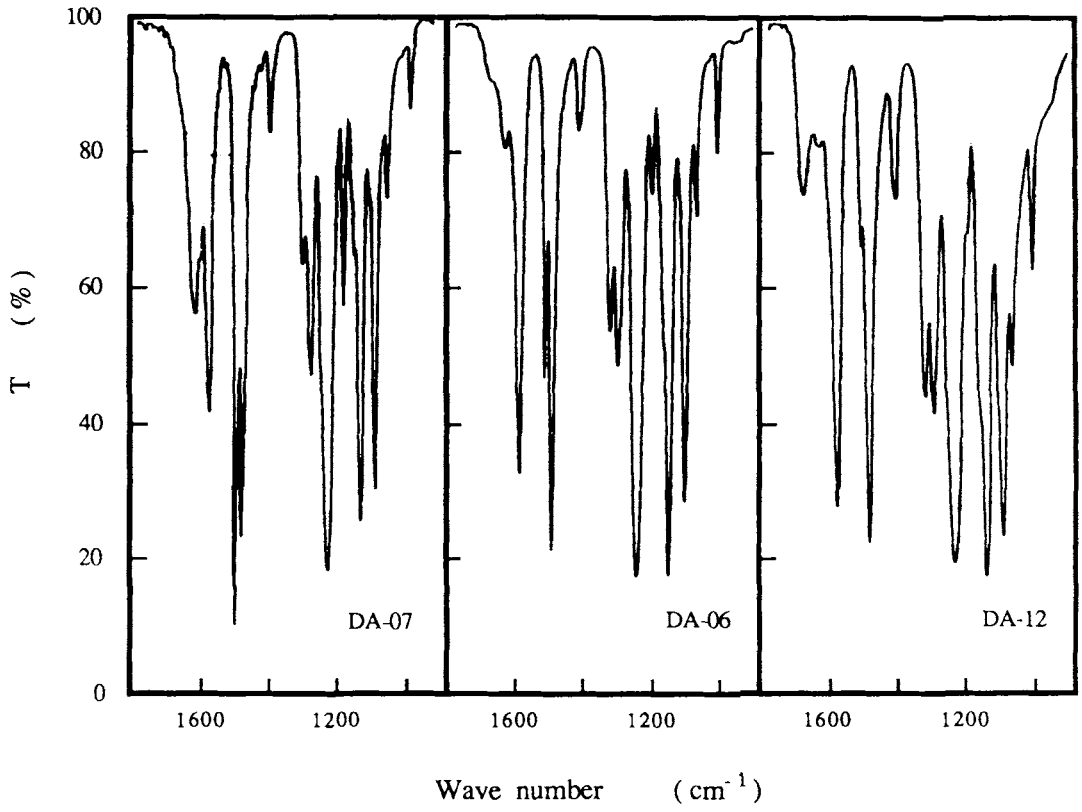


Figure 3 FT-IR of DA oligomers.

amine to cyclimide is well known.[21-24] The reaction is easy for an aliphatic amine and is relatively difficult for aromatic amines although the formation of amic acid is a quantitative reaction. The key to this reaction is imide cyclization, which is difficult to complete in the case of aromatic amines (only 30–56% yield). In order to solve this problem, some workers use sodium acetate,[25] acetic anhydride,[26] triethylamine, or ketene[27] to promote the cyclization reaction. Lyle, however, first synthesized imide-cyclized monomer (45% yield), then used this monomer as a terminating reagent in the polycondensation at 150°C for preparing the corresponding BMI oligomer.[14] The type of BMIPES that we want to prepare cannot be purified by normal separation methods and cannot be prepared by using Lyle's approach because the imide crosslinking reaction and addition reaction with carbonate acid take place simultaneously as the condensation reaction is carried out at 180°C. Therefore, we have to study the transformation of amic acid to maleimide. As we describe in Scheme 1, the cyclization reaction can be completed in two steps, where the first step is the formation of amic acid. Although this reaction is quantitative, there are *cis*- and *trans*-isomers of amic acid that are formed during the reaction. The *trans*-isomer, which is unable to cyclize, is the energetically favored product that is easy to form. In order to minimize the *trans*-product, the reaction must be carried out at lower temperatures, and acetic anhydride and triethylamine must be added to the reaction mixture to promote the cyclization reaction as soon as the first step reaction has finished. The uncyclized product, *trans*-amic acid, can be analyzed by a base–acid titration. Since the solution of the

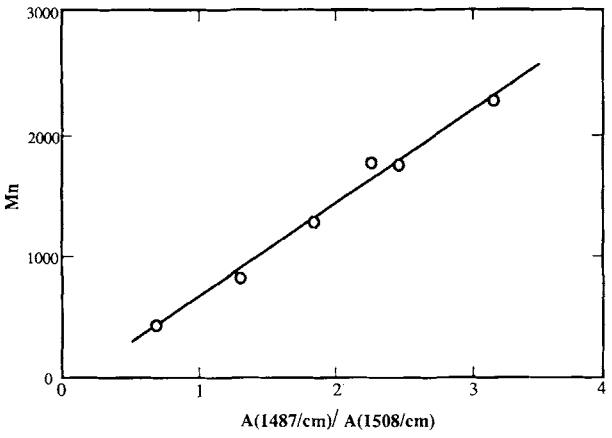


Figure 4 The relationship of IR data with DA M_n.

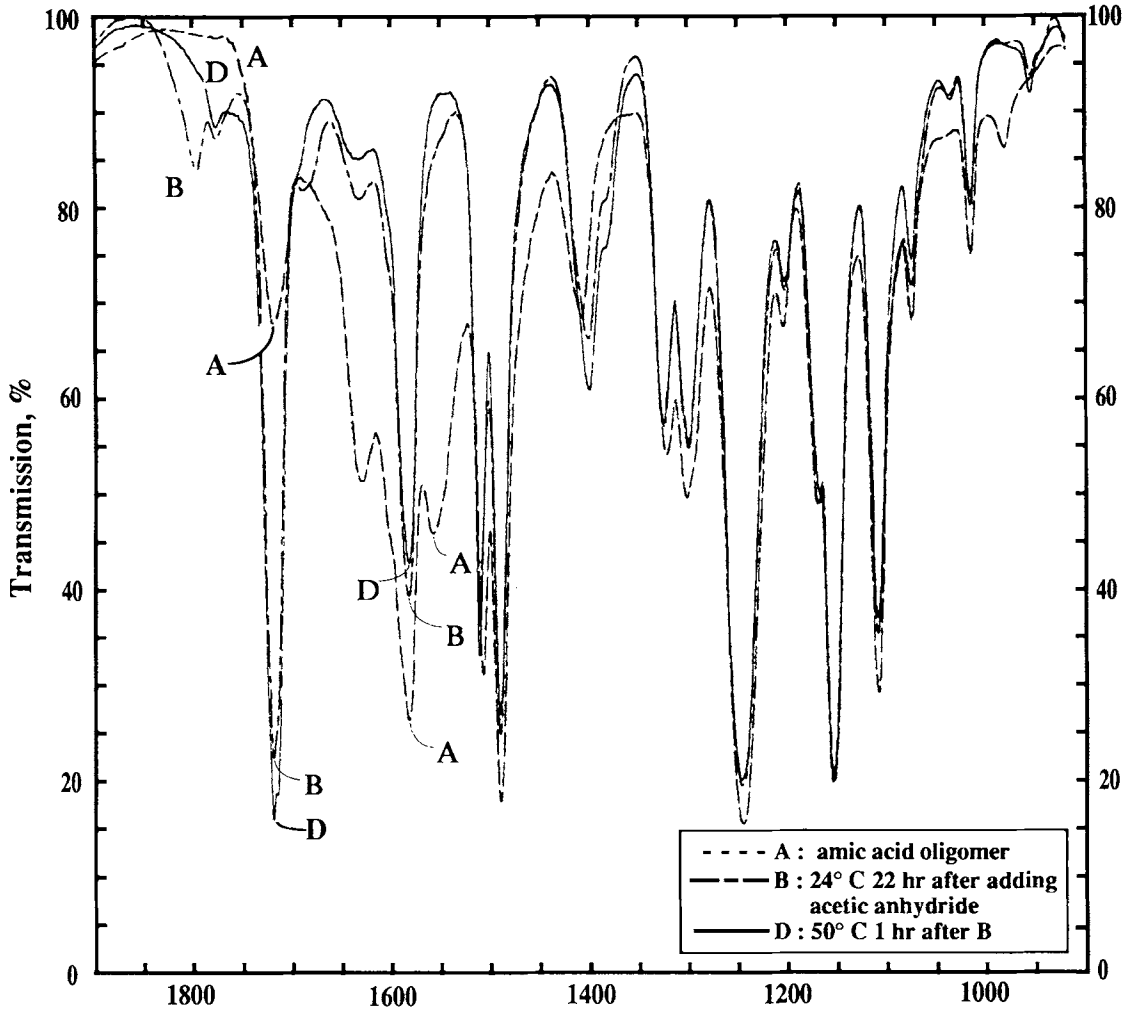


Figure 5 FT-IR of BMIPES oligomers (n = 2.8).

reaction product has a relatively deep color, it is difficult to determine the end point of titration by using indicators. Consequently, to monitor the titration a pH meter is preferred. The degree of cyclization can also be judged by using IR spectroscopy. The maleimide ring of these oligomers has the characteristic absorptions at 1720 and 1772 cm^{-1}. We notice that these two absorption peaks increased

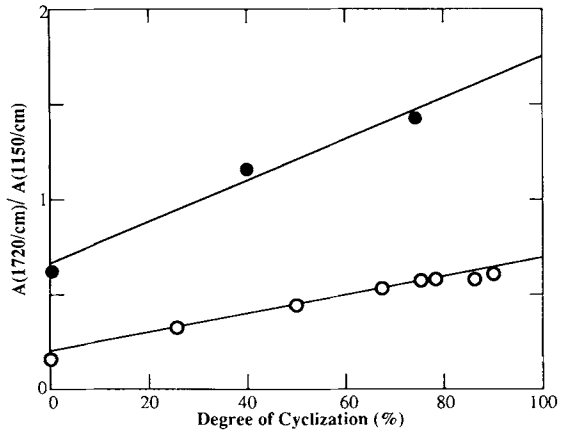


Figure 6 IR data vs. cyclization.

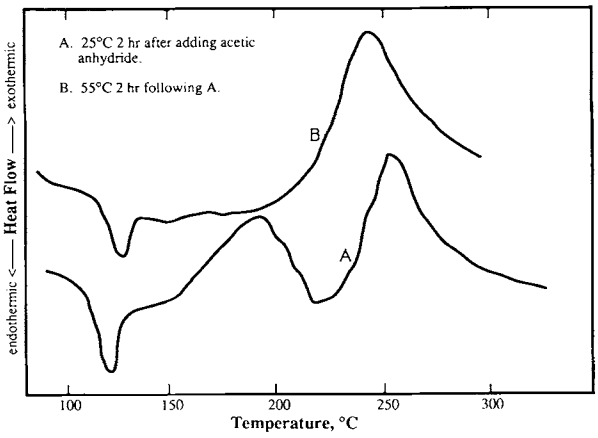


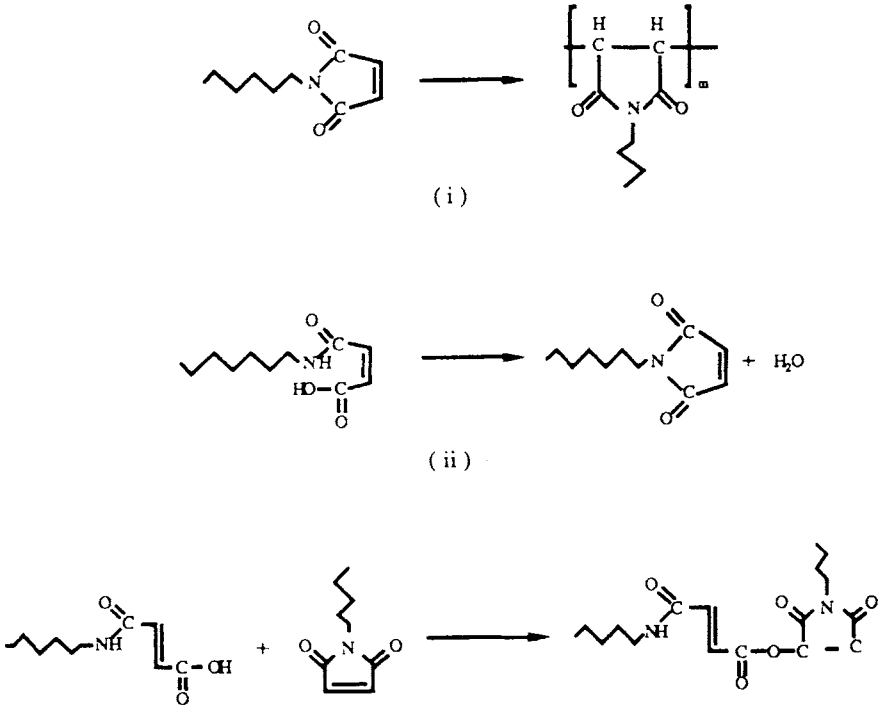
Figure 7 DSC traces of B-5.

Table III IR Data of Maleimide Cyclization

	$A_{1720\ cm^{-1}}/A_{1150\ cm^{-1}}$							
		20–24°C		50°C				
No.	AA 1–2 h	2 h	24 h	0 h	0.5 h	1 h	1.5 h	2.0 h
B-5	0.24		0.92		1.05	1.13		
B-6	0.18			0.70	0.74	0.69		0.70
B-8	0.16	0.61	0.69		0.67			0.63
B-3			0.56		0.62			
B-9	0.11			0.29	0.37		0.38	
B-10	0.09	0.33	0.35	0.38	0.40			

while the 1555 cm^{-1} peak due to amic acid decreased as the cyclization was carried out (see Fig. 5). If we use the 1850 cm^{-1} band as the base line and the $-SO_2-$ absorption at 1150 cm^{-1} as an internal standard, we can use relative absorption intensities at 1720 cm^{-1} as an indication of the degree of cyclization. Figure 6 shows that the results of this method fit perfectly the result obtained from the chemical titration. The results of imidization reaction of DA oligomers at room temperature are shown in Table III. To improve the degree of imidization, it was apparently not sufficient to simply prolong the reaction time at room temperature. We had to increase the temperature to 50°C for a short period in order to obtain the best results. Side reactions would occur at higher temperatures or longer times.

The DSC analysis of BMIPES oligomers is shown in Figure 7. The crosslinking reaction started at 200°C. During the curing process the main chemical reactions are shown in Scheme 3.



Scheme 3

Table IV Effect of Maleimide Cyclization on T_g (°C)[a] of Polymer[b]

			Maleimide Cyclization Condition						
			20–40°C		50°C				
No.	n	AA[c]	2 h	24 h	0 h	0.5 h	1 h	1.5 h	2 h
B-5	2.8	248	248	255		254	253		255
B-6	4.5	232	231		240	244	244		
B-8	6.8	202			215	214	210		212
B-9	8.9	223	222			225		223	
B-10	12.1		226	228		225			

[a] Determined by DSC, 20°C/min.
[b] Cured at 250°C for 4 h.
[c] Amic acid oligomer, the product of DA with maleic anhydride.

Reaction (i) is the expected reaction. Reaction (iii) is the addition reaction between acid and imide, which could occur under our reaction conditions. Reaction (ii) is a driven ring closure of amic acid, and many polyimide polymers are prepared by this type of ring closure. We observed this type of closure reaction by using DSC analyses as shown in Figure 7. The irregular thermoabsorption peak is due to the release of water during the ring closure reaction.

The T_g's of the reaction products after curing are determined by using DSC (Table IV). They range from 220°C to above 340°C and decrease as the molecular weight of the oligomers increase. Our results also indicate that the T_g's of polymers cured from mostly uncyclized amic acid oligomers are lower than those of mostly ring-closed maleimide oligomers. This means reaction (iii), which lowers the crosslinking density, did occur, but this effect is not very significant due to the occurrence of reaction (ii). It should be emphasized that although the cyclization of amic acid may not be very crucial to the quality of the final product, the small molecules, such as water released by further cyclization reaction, may create problems in the curing process. Therefore the cyclization to form imide must be controlled very carefully even though 100% conversion is not necessary.

Table V T_g (°C) of Cured BMIPES

Oligomers	Polymer		
M_n	I	II	III
600	> 340	> 330	
1000	255	239	
1500	244	185	177
2500	225		
5000			175
∞	220–230	190	165

In conclusion, we have synthesized maleimide-terminated poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) oligomers (BMIPES), which are light yellow to light gray powders at room temperature. They can be melted or softened below 200°C and are soluble in DMF, DMAc, DMSO, NMP, etc., polar solvents. Those oligomers with low molecular weight are also soluble in MEK and $CHCl_3$. They can be processed by means of the hot press and solution coating. They can self-condense above 200°C and form three-dimensional crosslinked networks. Compared to other BMIPS oligomers reported in the literature, they have higher T_g's (Table V) after curing. Therefore they are potentially more heat resistant and perhaps tougher (not too brittle) and may function well as the matrix resin of composites and adhesives.

This work was funded by a grant from the National Science Foundation (Material Research Group DMR 8708405).

Some preliminary experiments were carried out by Dr. Katheine A. W. McGrady. The authors thank Jaeyoung Jho for helpful discussions.

REFERENCES

1. F. Grundschober and J. Samboth, U. S. Pat. 3,380,964 April 30 (1968).
2. J. A. Parker, D. A. Kourtides, and G. M. Fohlen, in

High Temperature Polymer Matrix Composites, T. T. Serafini, Ed., Noyes Data Corp., Park Ridge, NJ, 1987, p. 54.
3. A. J. Kinloch and S. J. Shaw, *ACS, Polym. Mater. Sci. Eng.,* **49,** 307 (1983).
4. C. L. Segal, H. D. Stenzenberger, M. Herzog, W. Roemer, S. Pierce, and M. S. Canning, *17th National SAMPE Tech. Conf.,* Oct. 22–24, 1985, p. 147.
5. H. D. Stenzenberger, W. Roemer, M. Herzog, S. Pierce, M. Canning, and K. Fear, *31th International SAMPE Symp.,* April 7–10, 1981, p. 920.
6. H. D. Stenzenberger, P. Konig, M. Herzog, W. Romer, S. Pierce, and M. S. Canning, *32nd International SAMPE Symp.,* April 6–9, 1987, p. 44.
7. Boots Co., PLC, JP 62 27433; *Chem. Abstr.,* **107,** 199486 (1987).
8. R. H. Bott, J. D. Summers, C. A. Arnold, C. P. Blankenship, Jr., L. T. Tayor, T. C. Ward, and J. E. McGrath, *33rd International SAMPE Symp.,* March 7–10, 1988.
9. V. L. Bell and R. Young, *J. Polym. Sci. A,* **24,** 2647 (1986).
10. M. Bergain, A. Combet, and P. Grosjean, Br. Pat. 1,190,718 (1970).
11. D. A. Scola, *31st International SAMPE Symp.,* 1986.
12. G. T. Kwiatkowski, L. M. Robeson, G. L. Brode, and A. W. Bedrwin, *J. Polym. Sci. Polym. Chem. Ed.,* **13,** 961 (1975).
13. G. D. Lyle, D. K. Mohanty, J. A. Cecere, S. D. Wu, J. S. Senger, D. H. Chen, S. Kilic, and J. E. McGrath, *33rd International SAMPE Symp.,* March 7–10, 1988, p. 1080; also *Polym. Preprints,* **28**(1), 77 (1987).
14. G. D. Lyle, D. K. Mohanty, J. A. Cecere, S. D. Wu, J. S. Senger, D. H. Chen, S. Kilic, and J. E. McGrath, *Polym. Preprints,* **29**(1), 346 (1988).
15. A. B. Newton and J. B. Rose, *Polymer,* **13,** 465 (1972).
16. T. E. Attwood, A. B. Newton, and J. B. Rose, *Brit. Polym. J.,* **4,** 391 (1972).
17. Ger Offen. 2,731,816 (1979).
18. Br. Pat. 1,177,183 (1970).
19. JP 77 105,150 (1977).
20. JP 87,179,527; *Chem. Abstr.,* **108,** 38644 (1988).
21. L. E. Coleman, Jr., J. F. Bork, and Dunn, Jr., *J. Org. Chem.,* **24,** 135 (1959).
22. N. B. Mehta, A. P. Philips, F. Fu, Lui, and R. E. Brooks, *J. Org. Chem.,* **25,** 1012 (1960).
23. Y. P. Elliot, Ed., *Macromolecular Syntheses,* Vol. 2, Wiley, New York, 1966, p. 111.
24. U. S. Pat. 3,127,414 March 21 (1964).
25. Indra K. Varma and Shiromani Sharma, *Polymer,* **26,** 1562 (1985).
26. S. J. Shaw, *Mater. Sci. Tech.,* **3**(8), 589 (1987).
27. B. Lee, M. A. Chaudhari, and T. Galvin, *17th National SAMPE Tech. Conf.,* Oct. 22–24, 1985.

Received July 22, 1990
Accepted January 14, 1991