A new high pressure polymerization and simultaneous processing technique for the preparation of aromatic polycyanurates from aromatic dicyanate monomers

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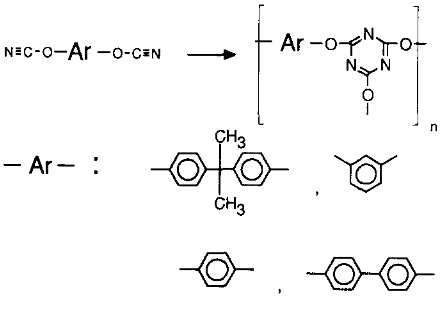
The high pressure polymerization of aromatic dicyanates was carried out by using a piston cylinder type hot-pressing apparatus, which led to the formation of crosslinked polycyanurate resins. In a model compound study, aromatic cyanates were found to cyclotrimerize under high pressure to give aromatic cyanurates, with the application of high pressure accelerating the cyclotrimerization process. Aromatic dicyanates polymerized at 150–280°C under pressures of 200–450 MPa, affording polycyanurates through a cyclotrimerization reaction. Polymerization under higher pressure required both higher temperatures and longer reaction times. After further curing of these crosslinked polymers, very hard resins were produced, with Vickers hardness values of 330–530 MPa and with a high modulus (>2 GPa), when compared with the same polymers synthesized under normal atmospheric pressure.

(Keywords: high pressure polymerization; aromatic dicyanates; polycyanurates)

INTRODUCTION

Aromatic polycyanurates are well known as excellent thermostable network polymers and have attained practical importance as adhesives, binders for laminates, casting resins, and for various other applications, particularly in the electronics and composites industries[1]. These polymers are readily prepared by the cyclotrimerization polymerization of aromatic dicyanates[2–9]. The most important aspect of the polymerization reaction of aromatic cyanates is that cyclotrimerization of the cyanate group is highly selective, resulting in a nearly quantitative triazine ring formation, when compared with other cyclotrimerization reactions, in which dimerization and chain polymerization can occur as side reactions[2,3,10,11]. Therefore, a number of attempts have been made to investigate the gel formation process which occurs during the cyclotrimerization polymerization of aromatic dicyanates[3,4,6–8]. These polymerizations have been carried out both in solution and in the absence of solvent, and have been promoted by the application of heat or by the use of catalysts such as zinc chloride.

Polycyanurates produced in this way are very difficult to process, since they have a crosslinked structure. In the field of synthetic polymer chemistry, the reactive hot pressing technique has been known for many years[12,13]. The basic concept of this technique is to simultaneously synthesize and mould intractable polymeric materials directly from the solid monomers, and it has been applied to the polymerization-processing of high-temperature aromatic polymers. The application of high pressure to cycloaddition reactions has been demonstrated to be an extremely effective technique, from both kinetic and thermodynamic considerations[14,15]. We have already reported the application of high pressure to the cycloaddition polymerization of *p*-cyanobenzonitrile *N*-oxide and found that the solid-state polymerization process at room temperature which gives poly(1,2,4-oxaziazole) was accelerated under high pressure[16]. This present investigation was undertaken in order to explore the high pressure polymerization and simultaneous processing of aromatic dicyanates to give crosslinked polycyanurates, without the use of any solvent or catalyst (see equation (1)).



(1)

EXPERIMENTAL

Apparatus

The apparatus used for the high pressure reaction has been described previously[16].

Monomer synthesis

Aryl cyanates were synthesized by the reaction of cyanogen bromide with the corresponding phenols in the

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presence of triethylamine, according to the method of Grigat and Putter[17], and were purified by distillation. Aromatic dicyanates were prepared from bisphenols by using the same procedure adopted for aryl cyanates[17]. After recrystallization from cyclohexane, all of the dicyanates were obtained in the form of colourless long needles. The i.r. spectra (KBr) exhibited characteristic absorption bands at 2200–2300 cm^{-1} (C≡N) and 1160–1235 cm^{-1} (C–O–C).

The following dicyanates were prepared in this work: 2,2′-bis(4-cyanotophenyl)propane (BADC), m.p. 79°C (lit. 80°C[17]); *m*-dicyanotobenzene (REDC), m.p. 76°C (lit. 80°C[17]); *p*-dicyanotobenzene (HQDC), m.p. 110°C (lit. 110°C[17]); 4,4′-dicyanotobiphenyl (BPDC), m.p. 137°C (lit. 131°C[17]).

Model reaction under high pressure

A typical example is given below. A portion of phenyl cyanate (0.5 g) was placed in a Teflon capsule (i.d. = 10 mm) and the capsule was then loaded into the cylinder of the hot-pressing apparatus. The piston cylinder was placed in the furnace, pressure was applied at room temperature to the capsule, and the temperature was then gradually increased. Reactions were carried out at various temperatures between 100 and 200°C, for 15 h, under pressures of 0.1–800 MPa. The reaction time was recorded from the point when the required temperature was reached, which usually took ~1 h. After the reaction was complete, the system was allowed to return to room temperature, and the pressure was then released to atmospheric. The product was isolated by washing with toluene and the resulting needle-shaped crystals were filtered and dried.

Polymerization under high pressure

A typical example of the polymerization process is as follows. A Teflon capsule (i.d. = 10 mm) was used for the polymerization of BADC (0.5 g), which was carried out at various temperatures between 200 and 340°C over periods of 5–40 h, under a pressure of 0.1–800 MPa, to give the aromatic polycyanurate. Polymer in the form of a flat cylindrical pellet, with a diameter of 10 mm and a thickness of 2–3 mm was produced in this way.

Polymerization and post-curing under high pressure

A typical example of this procedure is as follows. BADC was polymerized by using the method described above but in this case with reaction temperatures of between 200 and 280°C. After the reaction, post-curing was carried out at various temperatures over the range 280–340°C for 5–16 h under a pressure of 0.1–800 MPa, to give the polycyanurate in the form of a flat cylindrical pellet with a diameter of 10 mm and a thickness of 2–3 mm.

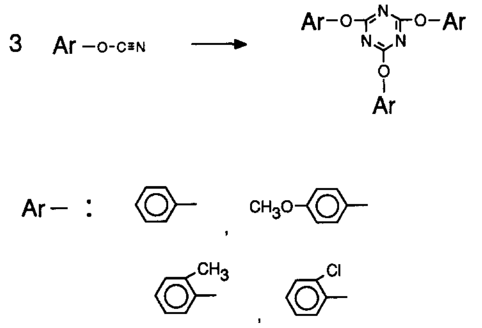
Measurements

I.r. spectra were recorded on a JASCO FTIR-5000 spectrophotometer. Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) were carried out using Shimadzu thermal analysers, DTA-40 and TGA-40 instruments, respectively. Dynamic mechanical analysis (d.m.a.) was carried out using a Toyoseiki Rheolograph Solid machine, operating at a frequency of 10 Hz, with a heating rate of 3°C min^{-1}. The specimen used had the following dimensions: 0.6 cm gauge length, 0.5 cm wide and 300–500 μm thick. The density of the polymers was measured by a conventional Archimedes displacement method, in water at 25°C. Vickers hardness measurements were carried out at room temperature using a Matsuzawa Seiki MHT2 microhardness tester, equipped with a diamond square pyramid, employing a load of 500 g applied for 15 s.

RESULTS AND DISCUSSION

Model reaction

Aryl cyanates are known to cyclotrimerize by heating, forming triaryl cyanurates (2,4,6-triaryloxy-1,3,5-triazines) in almost quantitative yields[17]. However, there have been no reports on the cyclotrimerization of aryl cyanates under high pressure, although high pressure is known to accelerate many organic reactions, including the trimerization of nitriles and phenyl isocyanate[11,12]. This work therefore represents the first investigation of the cyclotrimerization of aryl cyanates under high pressure (see equation (2)).



(2)

The high pressure reaction was carried out in the absence of both solvent and catalyst by using a piston-cylinder type hot-pressing apparatus. *Figure 1* shows the effect of pressure on the cyclotrimerization of phenyl cyanate, carried out at temperatures of 60 or 80°C for 15 h. Phenyl cyanate did not trimerize under atmospheric pressure at 60°C, but trimerized when high pressure was applied. As the applied pressure was

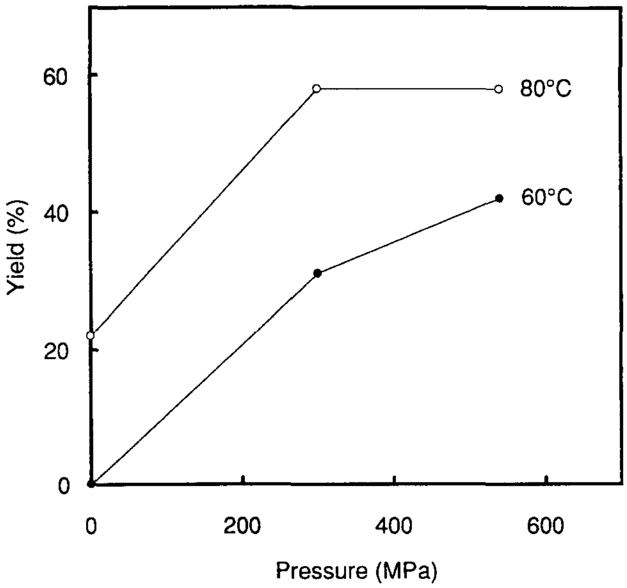
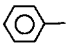
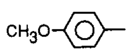
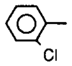
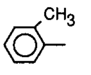


Figure 1 Effects of applied pressure and reaction temperature on the cyclotrimerization of phenyl cyanate: (●) 60; (○) 80°C

Table 1 Synthesis of aromatic cyanurates

Ar	Monomer m.p.^{a} (°C)	Reaction conditions P (MPa)	T (°C)	t (h)	Cyclotrimer M.p.^{a} (°C)	Yield (%)
		0.1	60	15		0
	Liquid	300	60	15	238	31
		540	60	15		42
		0.1	80	15	195	21
	26–28	200	80	15		59
		300	80	15		30
	Liquid	0.1	60	15		0
		400	60	15	171	25
	Liquid	0.1	80	15	161	52
		300	80	15		61
		500	80	15		80

^{a}Determined by d.t.a. at a heating rate of 10°C min^{-1}

increased, the yield of triphenyl cyanurate increased; yields were also improved by increasing the reaction temperature.

Table 1 shows the results of the high pressure cyclotrimerization of a number of aryl cyanates, where it can be seen that the reactions were accelerated effectively by the use of high pressure. One exception was the case of *p*-methoxyphenyl cyanate, where the yield of the cyclotrimer synthesized under a pressure of 300 MPa was lower than that of the trimer obtained using 200 MPa. This is probably associated with the high melting point of the cyanate (26°C), suggesting that this cyclotrimerization process only occurs to a small extent in the solid state. Therefore, high pressure cyclotrimerization reactions of aryl cyanates without the use of a solvent or catalyst were actually achieved by conducting them in the melt state.

High pressure polymerization of BADC

The above model reaction was extended to the high pressure polymerization-processing of aromatic dicyanates. BADC, a bisphenol A type dicyanate, was selected as a typical dicyanate monomer. In order to find the boundary conditions (i.e. the applied pressure and reaction temperature) for the cyclotrimerization polymerization reaction of BADC, polymerization was carried out under high pressure for 15 h without the use of solvent or catalyst; the results are shown in *Figure 2*. When a certain temperature was reached under a constant pressure, BADC polymerized to form transparent, light brown, and very hard crosslinked aromatic polycyanurate resin. Since this boundary temperature probably corresponds to the melting point of the monomer, the temperature required to cause polymerization increased with increasing the applied pressure. In other words, polymerization under higher pressures required higher temperatures. *Figure 3* shows the reaction time dependence of the glass transition temperature (T_g) (determined by d.m.a.) of the aromatic polycyanurate which was obtained by the polymerization of BADC under a pressure of 300 MPa at 220°C. As expected, a longer reaction time gave a higher-molecular-weight polymer, with a higher T_g value.

Figure 4 shows the effects of reaction temperature and applied pressure on the T_g of the aromatic polycyanurate obtained by the polymerization of BADC for a reaction time of 15 h. The T_g value of the polymer increased monotonically when increasing the reaction temperature, whereas it was reduced to lower values when the applied pressure was increased. In most cases, the T_g of the polymer was lower than the reaction temperature and, as the applied pressure increased, a higher reaction temperature was required to obtain polymer with the same T_g value. The results suggested that this polymerization process could occur in the rubbery state of the polymer. *Figure 5* shows the effects of the polymerization conditions on the Vickers hardness parameter of the polycyanurate. These results closely correspond to those obtained for the temperature and pressure dependences of T_g, as discussed above (see *Figure 4*). All of these results indicated that a higher pressure freezes the polymer molecular motion, and slows down the cyclotrimerization reaction of the cyanate moiety.

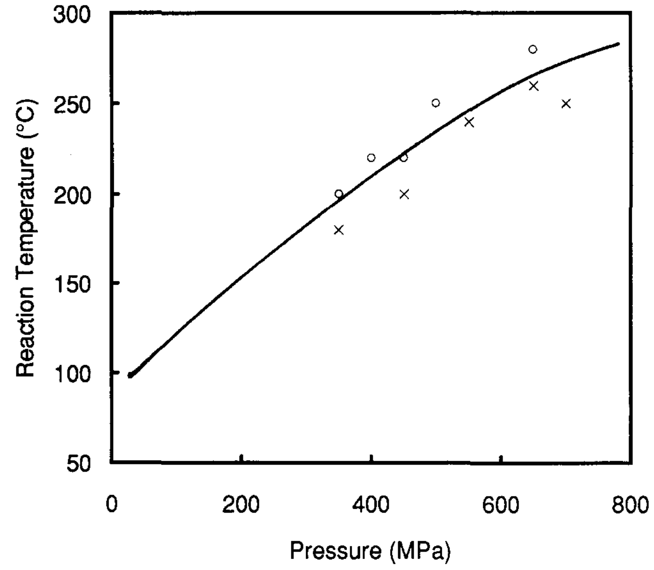


Figure 2 Boundary conditions for the polymerization of BADC for a reaction time of 15 h: (○) crosslinked polymer was obtained; (×) no reaction occurred

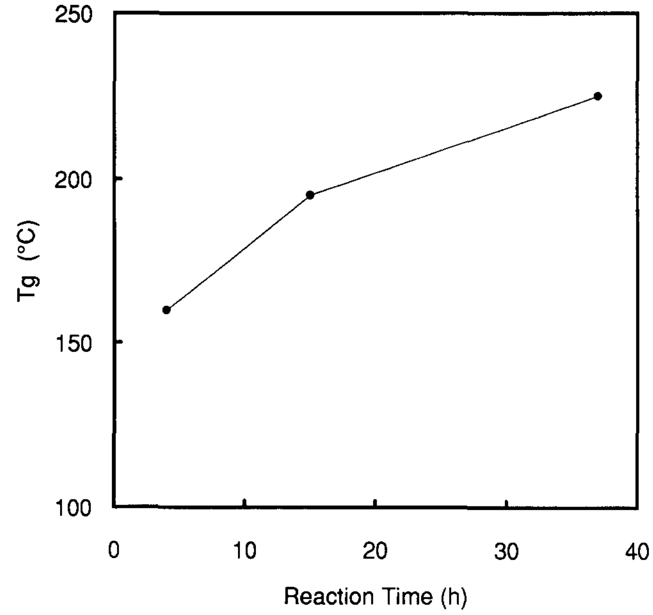


Figure 3 Reaction time dependence of the T_g of the aromatic polycyanurate formed by the polymerization of BADC under 300 MPa at 220°C

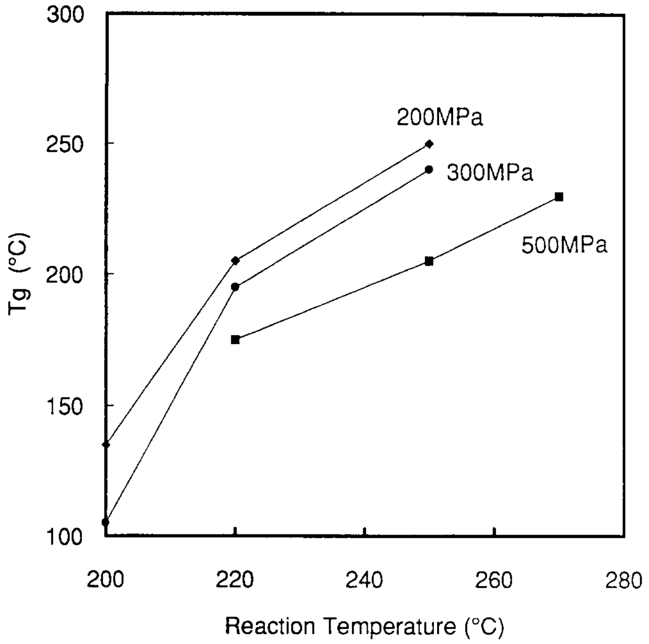


Figure 4 Effects of reaction temperature and applied pressure on the T_g of the aromatic polycyanurate formed by the polymerization of BADC for a reaction time of 15 h: (◆) 200; (●) 300; (■) 500 MPa

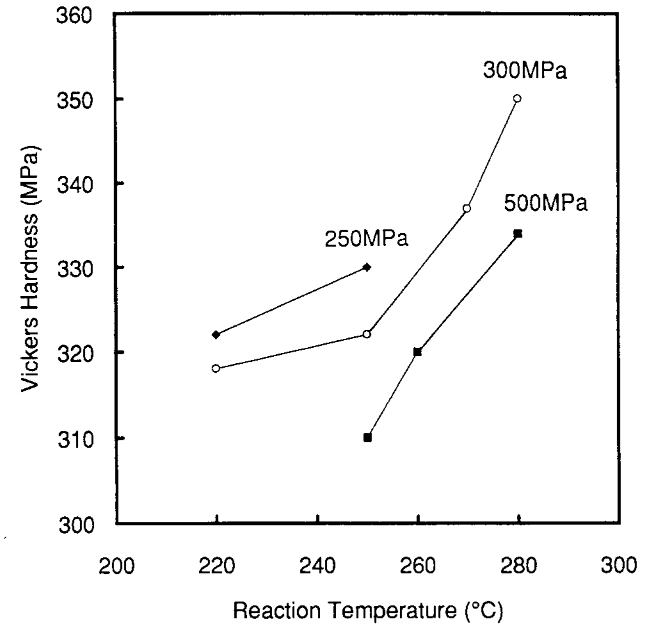


Figure 5 Effects of reaction temperature and applied pressure on the Vickers hardness (HV) parameter of the aromatic polycyanurate formed by the polymerization of BADC for a reaction time of 15 h: (◆) 250; (○) 300; (■) 500 MPa

We shall now discuss the polymerization behaviour of BADC in more detail, using results obtained from the dynamic mechanical analysis study. Curve A in *Figure 6* illustrates the dynamic mechanical properties of the polycyanurate formed by polymerization under atmospheric pressure at 240°C for 5 h in a sealed tube. The dynamic loss modulus (E'') curve of the polymer exhibited a rather narrow peak for the T_g at ~300°C, while the dynamic storage modulus (E') of the polymer showed only a slight decrease up to 300°C, suggesting that highly crosslinked polymer was obtained.

Curve B in *Figure 6* illustrates the dynamic mechanical properties of the polymer synthesized under a pressure of 300 MPa at 220°C. The storage modulus decreased gradually at temperatures of 150–200°C below the T_g, while the dynamic loss modulus exhibited a rather broad peak for T_g. It is suggested that low-molecular-weight, lightly crosslinked polymer was obtained by the high pressure polymerization. High pressure polymerization, carried out at a higher temperature, was expected to give higher-molecular-weight polymer. Curve C in *Figure 6* shows the dynamic mechanical properties of the polymer synthesized under a pressure of 300 MPa at 250°C. The dynamic storage modulus of this polymer slowly decreased up to 220°C, finally 'breaking down' at 280°C, while the dynamic loss modulus curve showed broad double peaks at 230 and 280°C. The results suggested that this resin was composed of both highly crosslinked and lightly crosslinked polymer. As the reaction temperature was increased, highly crosslinked polymer was rapidly formed to the same extent, so that the polymer acted as an interfering factor to the residual monomer, and thus fully crosslinked polymer was difficult to obtain directly under these high pressure and high temperature polymerization conditions.

High pressure polymerization of BADC and post-curing under high pressure

From the results of the dynamic mechanical analysis study of the high pressure polymerized polymer, it appeared that the high pressure polymerization process on its own was insufficient to produce a high T_g resin from BADC. Therefore, post-curing is necessary in order to complete the polymerization. *Figure 7* shows the d.m.a. curves of the polycyanurates formed after polymerization

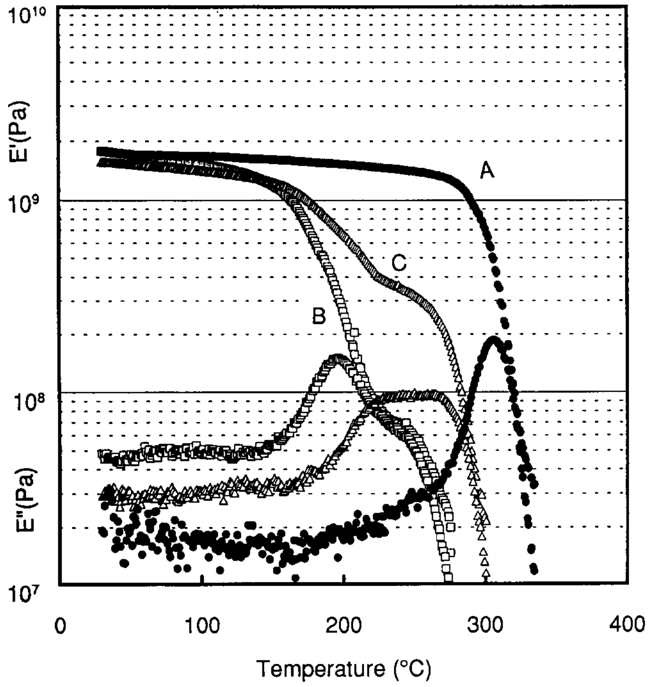


Figure 6 Temperature dependence curves of the dynamic storage modulus (E') and the dynamic loss modulus (E'') for the following aromatic polycyanurates derived from BADC: (A) the polymer produced at 240°C under 0.1 MPa for 5 h; (B) the polymer produced at 220°C under 300 MPa for 15 h; (C) the polymer produced at 250°C under 300 MPa for 15 h

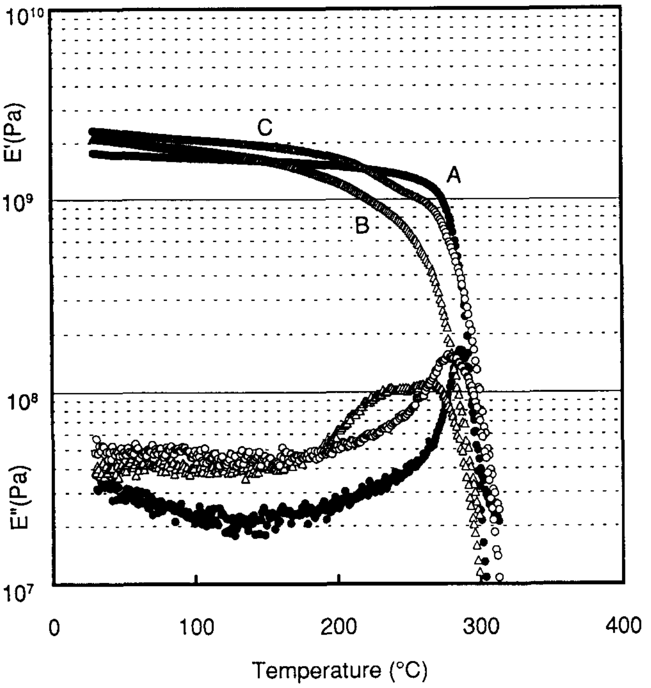


Figure 7 Temperature dependence curves of the dynamic storage modulus (E') and the dynamic loss modulus (E'') for the following aromatic polycyanurates derived from BADC: (A) the polymer produced at 180°C under 0.1 MPa for 15 h and then cured at 240°C for 5 h; (B) the polymer produced at 220°C under 300 MPa for 15 h and then cured at 280°C under 500 MPa for 5 h; (C) the polymer produced at 220°C under 300 MPa for 40 h and then cured at 280°C under 500 MPa for 5 h

of BADC for 15 h, followed by post-curing for 5 h. The conventional melt-processed polymer (curve A) was a fully crosslinked network polycyanurate resin, as evidenced by a slight decrease in the storage modulus as the temperature is increased up to the T_g (~300°C), with the latter corresponding to a sharp peak in the loss modulus curve. Curve B in *Figure 7* shows the results obtained for the polymer formed at 220°C under a pressure of 300 MPa for a reaction time of 15 h, and then cured at 280°C under a pressure of 500 MPa for a further 5 h. When compared with curve B in *Figure 6*, the cured polymer had a high T_g at ~250°C. However, it also showed thermal behaviour which was similar to that observed for the neat polymer when formed at high temperature and under high pressure (c.f. curve C in *Figure 6*), as shown by the decrease in the storage modulus and the broad double peaks of the loss modulus trace (curve B in *Figure 7*). This phenomenon was also observed for the long-period (15 h) cured polymer. These results suggested that it was difficult to obtain fully crosslinked polymer from lightly crosslinked low-molecular-weight material by post-curing, owing to restrictions of the polymer chain mobility under high pressure.

Curve C in *Figure 7* is the d.m.a. curve of the polymer formed by polymerization for a longer reaction time (40 h), in order to produce high-molecular-weight material, which was then post-cured. This polymer was found to be a fully crosslinked resin, as shown by a slight decrease in the storage modulus, a high T_g, and a single peak in the loss modulus curve, with features which were very similar to those of the polymer represented by curve A in *Figure 6*. All of these results again indicated that application of higher pressures retarded the cyclotrimerization polymerization of the aromatic dicyanate, so that a longer polymerization time, coupled with a high pressure post-curing treatment, was required, leading to the formation of a fully crosslinked polymer with a high molecular weight.

Additional characterization of the polymer involved the use of thermogravimetric analysis. Curve A in *Figure 8* shows a typical t.g.a. curve, measured in nitrogen, of the aromatic polycyanurate synthesized from BADC, under a pressure of 300 MPa at 220°C over a period of 15 h. The initial weight loss occurred at 185°C, followed by a further, gradual weight loss over the 200–400°C temperature range, which was probably due to the presence of lower-temperature-volatile components (i.e. unreacted monomer and low-molecular-weight oligomer). A further rapid weight loss was observed at 400–450°C, due to thermal decomposition of the polymer. After curing this polymer, under high pressure at 280°C for 5 h, the t.g.a. curve showed practically no weight loss up to 380°C, while a 10 wt% loss was recorded at 430°C (see curve B in *Figure 8*). Therefore, high pressure polymerization of the aromatic dicyanate alone was insufficient, and post-curing was necessary in order to complete the polymerization, thereby giving a polymer with good thermal stability.

High pressure polymerization of aromatic dicyanates and polymer properties

The reaction conditions used for the polymerization of four types of aromatic dicyanates, namely 2,2′-bis(4-cyanotophenyl)propane (BADC), *m*-dicyanotobenzene (REDC), *p*-dicyanotobenzene (HQDC), and 4,4′-dicyanotobiphenyl (BPDC), plus thermal and mechanical data of the resulting polymers, are summarized in *Table 2*. As the melting point of the monomer became higher, i.e. as the rigidity of the polymer backbone is increased, the polymerization process required both higher reaction and curing temperatures. Under a pressure of 300 MPa, polymerization occurred at a 20–30°C higher temperature, when compared with polymerization under atmospheric pressure. When the high pressure polymerizations were carried out at an elevated temperature (270–280°C), the polymers formed were less thermally stable, as indicated by their low initial decomposition temperatures. After curing at 280–320°C, all of the pressure processed polymer samples were stable up to 300°C and showed a

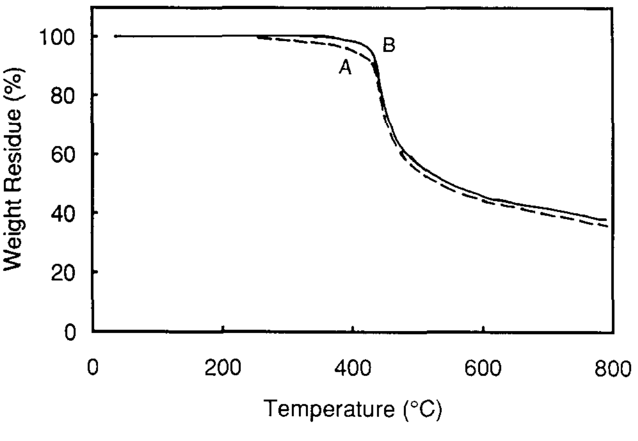
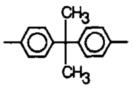
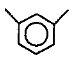
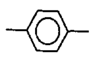
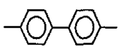


Figure 8 T.g.a. curves of aromatic polycyanurates derived from BADC, measured in nitrogen with a heating rate of 10°C min^{-1}: (A) the polymer produced at 220°C under 300 MPa for 15 h; (B) the same polymer after further treatment by curing under 500 MPa at 280°C for 5 h

Table 2 Reaction and curing conditions of various aromatic dicyanates plus mechanical and thermal data of the resulting polycyanurates

		Reaction conditions			Curing conditions			Polymer					
Ar	Abbreviation	P (MPa)	T (°C)	t (h)	P (MPa)	T (°C)	t (h)	d_{25}[a] ($g\,cm^{-3}$)	E'_{100}[b] (GPa)	T_g[c] (°C)	HV[d] (MPa)	T_i[e] (°C)	T_{10}[e] (°C)
	BADC	0.1	180	15	0.1	240	5	1.24	1.7	287	260	335	430
		300	220	15	–	–	–		1.5	195	320	185	430
		300	270	15	–	–	–		2.1	285	340	245	425
		200	220	40	350	280	5		2.1	280	330	310	435
	REDC	0.1	125	15	0.1	240	5	1.42	2.0	286	410	310	405
		200	150	40	200	250	5		2.1	270	430	310	405
	HQDC	0.1	200	15	0.1	250	5	1.43	2.2	–	–	330	445
		400	280	40	–	–	–		2.7	–	510	140	445
		300	220	40	350	280	5		2.2	>300	510	315	450
	BPDC	0.1	180	15	0.1	250	5		1.8	–	–	410	480
		350	280	40	–	–	–		1.9	–	410		
		450	270	15	450	300	5	1.35	1.8	>300	410	340	465

[a] Density of polymer at 25°C
[b] Dynamic storage modulus of polymer at 100°C
[c] Determined by d.m.a.
[d] Vickers hardness parameter
[e] T_i and T_{10} are initial decomposition temperature and 10%-weight-loss temperature, respectively, measured at a heating rate of 10°C min^{-1} in nitrogen

10 wt% loss at temperatures above 400°C, and the behaviour was very similar to that observed for the polymers synthesized under normal pressures.

The post-cured polymers had densities between 1.24 and 1.43 $g\,cm^{-3}$ and glass transition temperatures above 280°C. These values were consistent with the results reported previously for polymers that had been processed under normal pressures[18], and were thus independent of the reaction conditions employed. The storage modulus (measured at 100°C) increased in the following order of backbone unit, i.e. isopropylidenediphenylene, *m*-phenylene, and *p*-phenylene, which correlated well with the increasing order of rigidity of the polymer backbone. The polymers formed under conditions of high pressure had either the same or higher storage moduli, when compared with those formed under normal pressures. More remarkable, however, was the microhardness values of the polymers formed under high pressure conditions. The post-cured polymers that had been formed under high pressures had higher Vickers hardness values, when compared with the polymers processed at normal pressures. The increase in microhardness of the pressure processed materials was attributed to the fact that the application of pressure increased the packing density, thus giving more compact resins. This effect was more pronounced for the polymers with 'softer' polymer backbones, such as those derived from BADC. The Vickers hardness of the polymers increased with the increasing rigidity of the polymer backbone, and thus very hard resins, with Vickers hardness values of 510 MPa, were obtained from the *p*-dicyanotobenzene monomer.

CONCLUSIONS

Aromatic cyanates, when used in model compound studies, cyclotrimerized at 60–80°C under pressures of 100–500 MPa over a period of 15 h, affording aromatic cyanurates. This reaction was accelerated under high pressure. Aromatic dicyanates polymerized at 150–280°C under pressures of 200–450 MPa to give polycyanurates through a cyclotrimerization reaction. Polymerization using higher pressures required higher temperatures and longer reaction times. This suggested that the polymerization reaction became diffusion-limited under high pressure conditions and hence the reaction rate decreased. In addition, after further curing at 250–300°C under pressures of 200–450 MPa, these crosslinked polymers gave very hard resins with Vickers hardness values of 330–530 MPa, high moduli (>2 GPa), stability up to 300°C, and high glass transition temperatures (>280°C).

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REFERENCES

1 Shimp, D. A. *SAMPE Q.* 1987, **19**, 41
2 Pankratov, V. A., Vinogradova, S. V. and Korshak, V. V. *Russ. Chem. Rev.* 1977, **46**, 278
3 Korshak, V. V., Pankratov, V. A., Ladovskaya, A. A. and Vinogradova, S. V. *J. Polym. Sci. Polym. Chem. Edn* 1978, **16**, 1697
4 Bauer, M., Bauer, J. and Kuhn, G. *Acta Polym.* 1986, **37**, 715
5 Penczek, P. and Kiminska, W. *Adv. Polym. Sci.* 1990, **97**, 41
6 Osei-Owusu, A., Martin, G. C. and Gotro, J. T. *Polym. Eng. Sci.* 1991, **31**, 1604
7 Gupta, A. M. and Macosko, W. *Makromol. Chem. Macromol. Symp.* 1991, **45**, 105
8 Williams. R. J. J., Vazquez, A. and Pascault, J. P. *Polym. Bull.* 1992, **28**, 219
9 Papathomas, K. I. and Wang, D. W. *J. Appl. Polym. Sci.* 1992, **44**, 1267

10 Patai, S. 'The Chemistry of Cyanates and Their Thio Derivatives', Wiley, New York, 1977

11 Grigat, E. and Putter, R. *Angew, Chem. Int. Edn Engl.* 1967, **6**, 206

12 Morgan, P. E. D. and Scott, H. *J. Polym. Sci., B* 1969, **7**, 437

13 Morgan, P. E. D. and Scott, H. *J. Appl. Polym. Sci.* 1972, **16**, 2029

14 Matsumoto, K., Sera, A. and Uchida, T. *Synthesis* 1985, 1

15 Matsumoto, K. and Sera, A. *Synthesis* 1985, 999

16 Itoya, K., Kakimoto, M., Imai, Y. and Fukunaga, O. *Polym. J.* 1992, **24**, 979

17 Grigat, E. and Putter, R. *Chem. Ber.* 1964, **97**, 3012

18 Korshark, V. V., Pankratov, V. A., Askadskii, A. A., Puchin, A. G. and Vinogradova, S. V. *Polym. Sci. USSR* 1974, **16**, 1133