Mechanical and Thermal Properties of Polyquinolines

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ABSTRACT: The glass-transition, melt, and thermal-decomposition temperatures of a series of 16 polyquinolines were determined by DSC. Intramolecular effects such as molecular symmetry, steric crowding, and the presence of flexibilizing groups in the chain on the thermal behavior of these polymers were investigated. Depending on the structure of the repeat unit, the glass-transition temperatures varied from 266 to 415 °C. Melting of the crystalline regions takes place between 448 and 552 °C depending on the structure, and the T_g/T_m ratio increases from 0.75 to 0.84 with increasing chain stiffness. The static mechanical and dynamic mechanical properties of a few selected polymers were also determined. The tensile strengths of films at room temperature were 4 to 7 × 10^3 psi. The dynamic tensile storage modulus of completely amorphous films increased from 2 to 5 × 10^{10} dyn/cm^2 with increasing chain stiffness. Annealing the films above T_g results in a threefold increase in Young's modulus and is attributed to the development of ordered phases in these materials.

The majority of the thermally stable polymers as yet have not achieved commercial importance as a result of: (1) limited or nonexistant information about the physical and mechanical properties; (2) the difficulty of processing these materials in the bulk on conventional, commercially available equipment; (3) the limited solubility in conventional organic solvents; (4) their relatively high projected manufacturing cost. The last factor is probably the most serious and may well limit the application of these materials to specialty cases. Processing and solubility limitations may eventually be overcome by proper synthetic methods and structure tailoring techniques. It was the objective of this study to provide information on the physical and mechanical properties of one family of high-temperature polymers, the polyanthrazolines and polyquinolines, whose syntheses have been described in three previous papers.[1-3]

Experimental Section

A Du Pont Model 990 thermoanalyzer was used to determine glass, melt transitions, and thermal-decomposition temperatures as well as the change in specific heats in the glass-transition intervals. An Instron mechanical tester was employed to determine the static mechanical properties, and a Vibron DDV-II was used to measure the dynamic mechanical properties of solution cast films. Unless specified, all measurements were made in inert atmospheres at heating rates listed in the tables. As shown in Figure 1, for polymer **11** (Table I), the nature, extent, and location of the glass-transition interval is strongly dependent on thermal history. In order to permit a valid comparison of the T_g of various polymers, all samples were heated above T_g and subsequently quenched into liquid nitrogen. Samples prepared in this way did not exhibit melt transitions. However, with the exception of polymers **15** and **16**, all samples which were used as received after synthesis without quenching did show endothermic melting peaks by DSC. The intensity of these peaks varied from one polymer to another and by far the most intense melting curves were obtained for polymer **1**, which also exhibited the highest degree of x-ray crystallinity.

Instron testing of films was carried out with dog bone specimens 1 in. in length and ⅜ in. in width at the center of the specimen. Each point of the data shown in Figure 2 represents the average value based on three tests. There was considerable scatter in the individual values due to the fact that film specimens failed by combination of tear and tensile stress. For this reason, and because the films prepared were not optimized with respect to solvents and casting parameters, the values reported here are preliminary and obviously do not reflect the ultimate mechanical strength properties. However, DSC scans of film specimens show no evidence of residual solvent. The dynamic mechanical properties of two polyquinolines (Figure 3 and Figure 10, ref 5) were determined as follows using the Rheovibron (Model DDV-II): Samples were cut into narrow strips 2 cm in length approximately 0.40 ± 0.01 cm in width, and 0.004 ± 0.0005 cm in thickness. Runs were made at a frequency of 35 Hz at a heating rate of 5 °C/min in an inert sample atmosphere. The reproducibility of two runs was ±3%. The dynamic moduli of films were calculated using the following equation:

$$|E^*| = \frac{2}{(A)(\mathrm{DF} - K)} \frac{L}{S} 10^9 \text{ dyn/cm}^2$$

Where A is a constant given by the instrument manual,[4] DF is the value of the dynamic force dial when measuring tan δ, L is the length of sample, S is the cross-sectional area in cm^2, and K is an error constant due to the modulus of electricity and displacement of the stress gage. This value was experimentally determined for polyquinolines and found to be 40, and was independent of temperature. Values of Young's modulus E' and the loss modulus E'' were obtained as follows:

$$E' = |E^*| \cos \delta$$

and

$$E'' = |E^*| \sin \delta$$

Discussion

T_g and T_m. In a previous paper[5] it was established that the thermal behavior of polyquinolines is strongly affected by thermal history. It was suggested that these polymers not only are composed of two phases, one crystalline, the other noncrystalline, but also that within the noncrystalline phase there apparently exist multiple subphases, which in their glass-transition interval exhibit distinct first-order transitional behavior. So, in a microscopic sense, these materials can be considered composites or multiphase alloys. Furthermore, it was found that polyquinolines, even under ambient conditions several hundred degrees below their glass-transition temperatures are subject to continuous change or reorganization, and that within practical time scales, equilibrium is never achieved. In the discussion following it is important to realize that some properties assigned to these polymers such as Young's modulus cannot be considered materials constants, but, as will be hopefully demonstrated in future publications, are nonequilibrium, time-dependent variables. What has been said so far is of course not new information. Surprising are the observations that polyquinolines undergo structural rearrangements at temperatures far below their T_g's and that these rearrangements which take place in the amorphous phase reach such relatively high magnitudes.[5] This situation is unfortunate, for it means that definite properties may never be assigned to these materials.

The data in Table I show thermal transition temperatures for 16 polyquinolines of different chemical repeat unit structures. The polymers shown were arranged into groups of simular structures. Within each group, polymers were generally listed in order of decreasing T_g.

Polymer **1** in Table I is different from the others in that it was synthesized via its A–B monomer.[3] This particular route leads to a relatively simple chemical structure where all quinoline groups are linked together by one type of bond only. Therefore, all chain-connecting units are separated by identical bond angles. This should yield a very regular chain con-

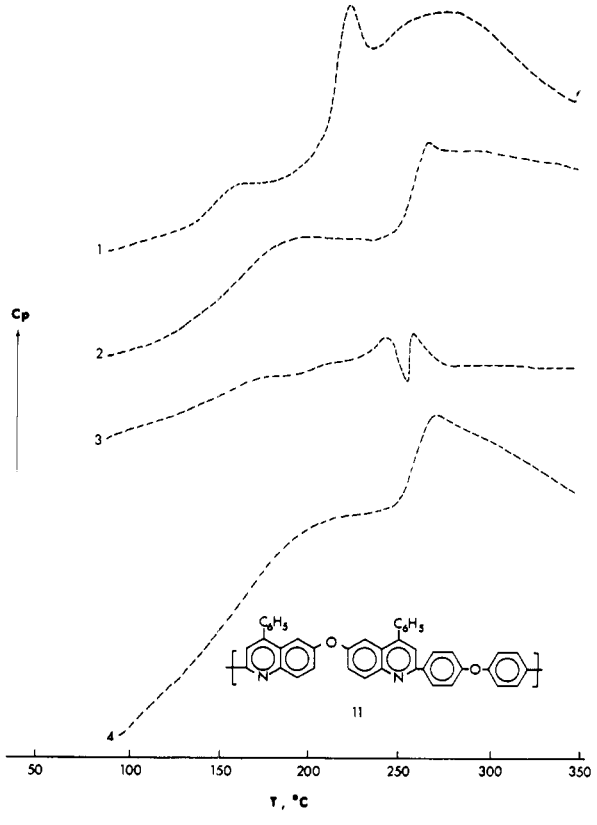


Figure 1. DSC curves of polymer 11 (Table I), 12-mg samples: (1) semicrystalline film, oriented; (2) amorphous film after quenching at ~1000 °C/s into LN_2; (3) powder; (4) powder after quenching as in (2).

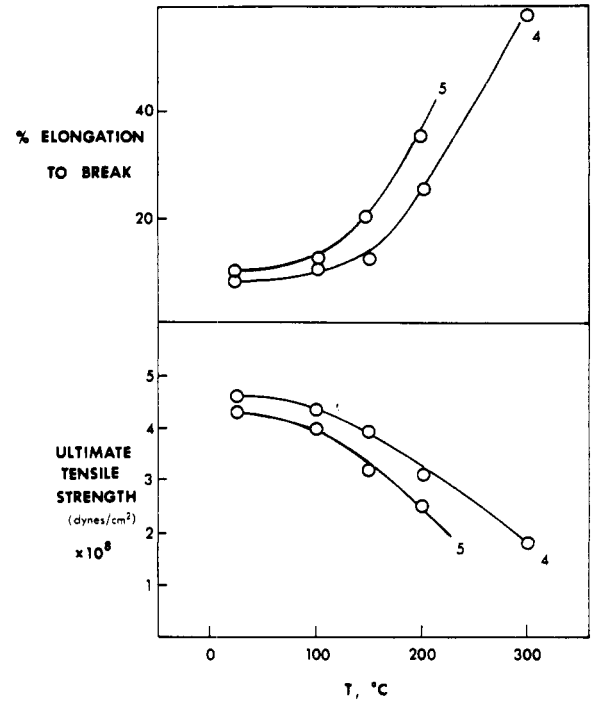


Figure 2. Mechanical properties of polymers 4 and 5 as a function of temperature.

formation, which is a prerequisite for the development of crystallinity. This was found to be the case. The x-ray crystallinity of this polymer which crystallized out during polymerization[3] was about 65%, while all other polymers were less that 20% crystalline. The glass-transition temperature of this

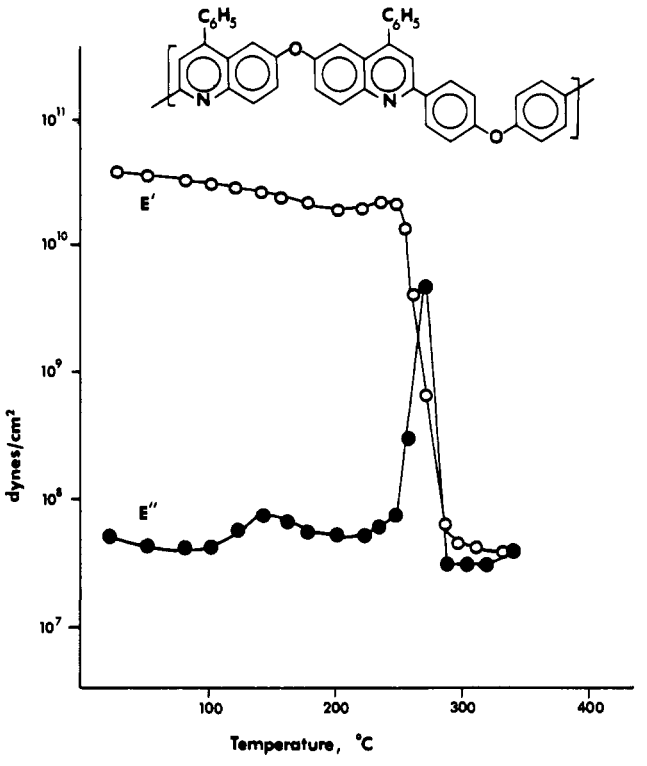


Figure 3. Dynamic storage and loss modulus vs. temperature: heating rate 5 °C/min; He atmosphere; frequency, 35 Hz.

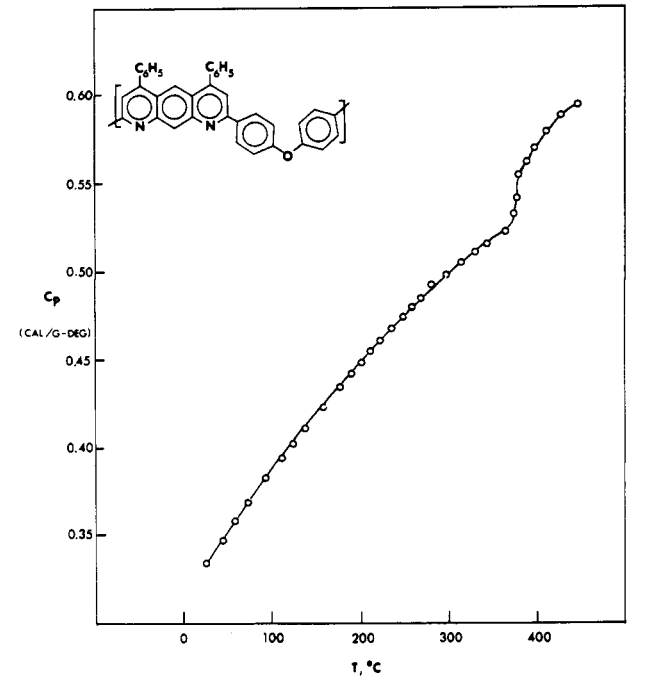


Figure 4. Specific heat as a function of temperature for polymer 4 (Table I).

material was 415 °C, which was higher than any other polymer listed in Table I and it was detected by DSC only at an extremely high instrument sensitivity (0.02 °C/in. of chart paper). The melting point of the crystalline phase of polymer 1 was at 552 °C, about 50 to 100 °C higher than that of the other polymers. The higher melting point of this polymer is very likely due to the presence of more perfect crystals.

Polymers 2–16 in Table I are of the AA–BB type; they were mainly amorphous and there was good correlation between their intramolecular structure and T_g. (For a general discus-

Table I: Thermal Properties of Polyanthrazolines, Polyisoanthrazolines, and Polyquinolines

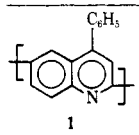
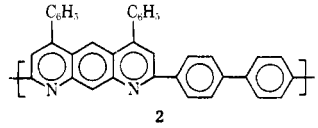
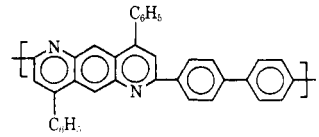
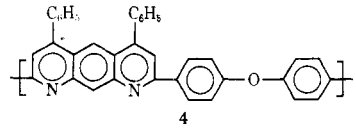
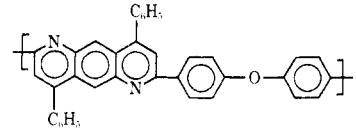
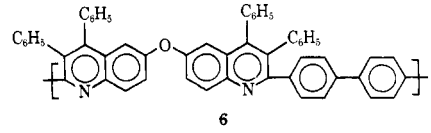
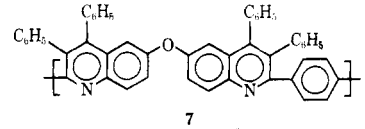
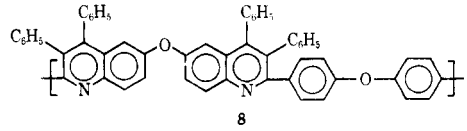
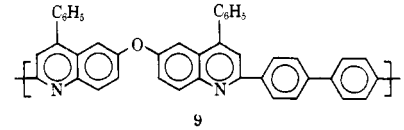
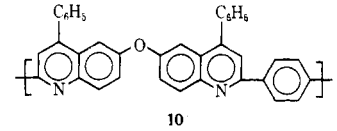
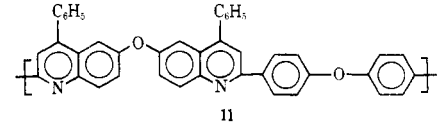
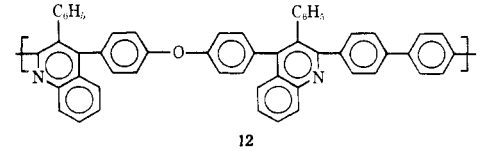
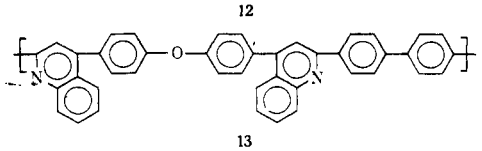
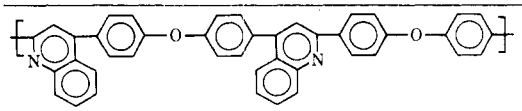
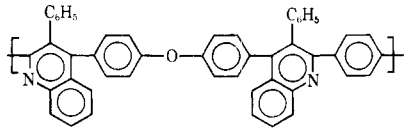
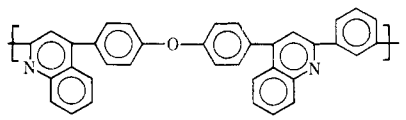
	η_{inh}	T_g, °C	T_m, °C	T_g/T_m	T_D, °C	$(\Delta C_p)_{T_g}$, cal/(mol deg)
 1	2.2	415	552	0.83	580	
 2	0.62	392	513	0.85	580	3.90
 3	0.89	383	498	0.85	580	4.15
 4	0.77	379	502	0.84	540	3.60
 5	0.59	362	490	0.83	540	3.80
 6	4.10	351	480	0.83		5.10
 7	3.40	345	475	0.82		6.0
 8	2.00	305	476	0.77		5.20
 9	3.10	308	480	0.77		4.00
 10	1.10	300	455	0.79		3.85
 11	1.80	266	448	0.75		3.00
 12	0.57	345	500	0.80	540	4.10
 13	0.38	326	475	0.80	575	

Table I (continued)

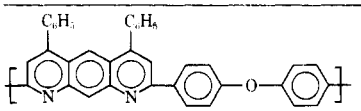
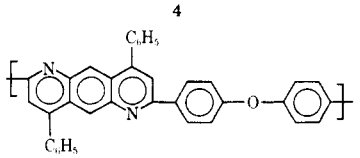
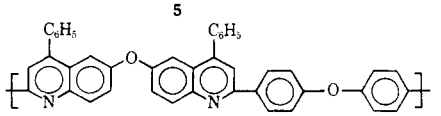
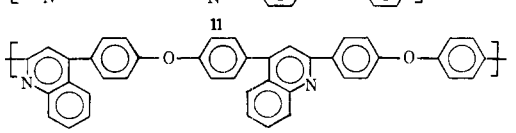
	η_{inh}	T_g, °C	T_m, °C	T_g/T_m	T_D, °C	$(\Delta C_p)T_g$, cal/(mol deg)
 14	0.62	276	483	0.73	565	4.95
 15	0.26	273	AMORPH		520	
 16	0.36	268	AMORPH		520	

sion on the effects of molecular structure on T_g in polymers the leader is referred to in ref 7 and 8.) The results may be summarized as follows: (1) The completely aromatic nature of these polyquinolines is responsible for their high T_g's (>260 °C). (2) Polymers with three fused aromatic rings (**2–5**) exhibit T_g's about 100 °C higher than their respective analogues containing two fused rings (**9–11**). (3) Geometric isomerism affects T_g. A comparison of polymers **2** with **3** and **4** with **5** showed that the isoanthrazoline structures (**2** and **5**) exhibit T_g's about 10 °C below their anthrazoline isomers. (4) Phenylation increases T_g (compare polymers **12** with **13** and **15** with **16**). (5) Steric hindrance increases T_g. The substitution of phenyl groups (**6, 7, 8**) in place of H atoms (polymers **9, 10,** and **11**) increases T_g by about 50 °C. (6) Flexibilizing ether groups decrease T_g by 30–50 °C. (Compare **6** with **5, 9** with **11,** and **13** with **14.**) The jump in specific heat at T_g per flexible bond was calculated as previously described.[6] As with other aromatic polymers, ΔC_p's for polyquinolines were significantly higher than expected by the rule of constant C_p. (See the example in Figure 4.)

The effect of the structure of the recurring unit on the melting points of polyquinolines was less pronounced. In fact there was no clear correlation between structure and T_m, and with the exception of polymer **1**, the majority of polyquinoline melted between 480 and 500 °C. While the high melting points per se are attributed to the rigid ring structure which increases the entropy of fusion, the relative constancy of T_m of structurally different polyquinolines is probably due to their low degree of crystallinity, and crystal perfection. In fact except for polymer **1** it is not certain that the endothermic peaks observed are due to a heat of fusion. Alternatively, these endotherms could be heat of dissolution of crystalline regions into the liquid amorphous regions with the dissolution temperatures to be similar for different polyquinolines. A quantitative study of the crystallization and melt behavior of polyquinolines is presently underway which will establish (1) the extent to which these polymers can be crystallized and (2) the effect of annealing on melting.

Thermomechanical Properties. The ultimate tensile strength and break elongation of polymers **4** and **5** (Table I)

Table II
Thermomechanical Properties of Polyquinolines[a]

	$[\eta]$	T_g, °C	$T_{E''max}$,[b] °C	$E'_{25°C}$, dyn/cm²	E' above T_g
 4	0.51	379	382	4.8×10^{10}	7.2×10^{7}
 5	0.53	362	368	3.5×10^{10}	2.4×10^{7}
 11	0.94	266	271	2.3×10^{10} (6.1×10^{10})	2.4×10^{7} (9.0×10^{7})[a]
 14	0.62	276	300	1.9×10^{10}	1.1×10^{7}

[a] Annealed above T_g (280 °C) for 2 h followed by cooling at a rate of 0.5 °C/min. [b] Applied frequency = 35 Hz.

were measured as a function of temperature (Figure 2). The data show that at high mechanical stresses, plastic deformation takes place in these polymers far below their glass-transition temperatures. For example, the film elongation at break for polymer **4** at 300 °C, 80 °C below T_g, is 60%, and the tensile strength at this temperature has decreased by a factor of about 3. The results indicate that when these polymers are to be used as load bearing materials their use temperatures lie significantly below their respective T_g or T_m, a phenomena which is not always appreciated in the application of these polymers for use as structural materials.

Under mild tensile stresses as required for dynamic mechanical testing (Figure 3 and Figure 10, ref 5) the mechanical performance of films is as expected relatively constant up to the glass transition temperature. Above T_g mechanical losses become pronounced as effected in a drop in Young's modulus from 2–5 $\times 10^{10}$ to less than 10^7 dyn/cm^2. This behavior is typical for noncrystalline, linear high polymers. Mechanical losses of low amptitude are observed in polyquinolines between 100 and 150 °C (Figure 3 and Figure 10, ref 5). While the nature of these losses is presently not understood, we have observed these peaks also in polyimides, polyquinoxalines, polyphenylene ethers, and poly-*as*-triazines, and they are apparently common to most aromatic polymers.

In Table II are listed dynamic mechanical data for four different polyquinolines. It is noted that Young's modulus decreases from 4.8×10^{10} dyn/cm^2 for the more rigid polymer **4** to 1.9×10^{10} dyn/cm^2 for polymer **14** which contains an additional flexibilizing diphenyl ether linkage between the quinoline groups. The effect of annealing films above T_g on Young's modulus was shown for polymer **11** (Table II). A film sample which was annealed at 280 °C for 2 h followed by cooling at a rate of 0.5 °C/min had a Young's modulus of 6.1×10^{10} dyn/cm^2 as compared to the value of 2.3×10^{10} for the original film sample. Both samples were essentially x-ray amorphous and the threefold increase in modulus was attributed to ordering of the amorphous material.

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References and Notes

(1) Y. Imai, E. F. Johnson, T. Katto, M. Kurihara, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2233 (1974).
(2) J. F. Wolfe and J. K. Stille, *Macromolecules*, **9**, 489 (1976).
(3) S. O. Norris and J. K. Stille, *Macromolecules*, **9**, 496 (1976).
(4) Rheovibron Mod. DDV-II Instruction Manual 14, August 1969, Tape Measuring Instrument Co., Ltd.
(5) W. Wrasidlo and J. K. Stille, *Macromolecules*, **9**, 505 (1976).
(6) W. Wrasidlo, *J. Polym. Sci., Part A-2*, 1603 (1971).
(7) R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
(8) M. C. Shen and A. Eisenberg, *Prog. Solid State Chem.*, **3**, 407 (1966).
(9) J. Heijboer, *Plastica*, **19**, 489 (1966).

The Cross-Linking of Thermally Stable Aromatic Polymers by Aryl Cyanate Cyclotrimerization

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ABSTRACT: Thermally stable aromatic polymers have been cross-linked by employing the cyclotrimerization of aryl cyanates as the curing reaction. Biscyanato prepolymers of a phenylated polyphenylene and a polyphenylquinoline were synthesized by the reaction of cyanogen bromide with the corresponding hydroxyl end-capped oligomers. Thermal treatment of these prepolymers afforded a three-dimensional network structure with cyanurate ring structures at the cross-linking site. The cured polymers showed an increase of T_g over that of the corresponding biscyanato prepolymers. These values of T_g did not exceed those of the parent polymers because of the copolymer effect induced by the presence of the cyanurate structures. These materials were insoluble and showed thermal stabilities characteristic of the parent polymer systems, although initial weight losses of 4–8% above 400 °C were shown to be caused by the loss of cyanuric acid from the cross-linking sites. Hydrolytic stabilities of these materials were very good in acidic or basic aqueous media, but complete degradation of the cross-linking structures occurred in a strongly basic, swelling solvent medium.

The processability of thermally stable aromatic polymers is often quite limited because of the high values of T_g usually exhibited by these polymers.[1] The incorporation of flexible structures in the polymer chain makes processing more amenable by lowering the T_g. However, this modification also lowers the use temperature well below the thermal capability of the polymer as defined by the degradation temperature.

The softening point of a polymer (T_g) can be raised or eliminated by the formation of a network structure. However, there is no general method for introducing cross-links in the relatively inert, totally aromatic or heterocyclic polymer during or after fabrication. Ideally, a cross-linking reaction which is suitable for thermally stable polymers must produce a thermally stable link which is hydrolytically stable, and compatible with the polymer system. Also, it should proceed quantitatively, produce no volatiles, and occur under thermal or catalytic conditions, but not in storage. A reaction which approaches these requirements is the cyclotrimerization of aryl cyanates.

Although cyanates have been synthesized by several different methods,[2] the most convenient route[3] involves treating a phenol **1** and a cyanogen halide **2** with the stoichiometric amount of triethylamine to afford a quantitative yield of the aryl cyanate **3** (Scheme I). Although alkyl cyanates readily undergo rearrangement to the corresponding alkyl isocyanates, **3** is stable[2] and is isolable by distillation or crystallization.

Quantitative yields of trisaryl-*s*-triazine (aryl cyanurate) (**4**) have been obtained from the cyclotrimerization of **3**.[2–4] The reaction is promoted by heat, protonic acids, Lewis acids, and bases,[2,5,6] and can be carried out in a number of solvents or neat.[6] The trimerization of cyanates is highly selective when compared with other cyclotrimerization reactions in which chain polymerization and dimerization compete as side reactions.[6] The phenyl cyanurate **4** (Ar = Ph) has been reported[7,8] to be relatively chemically inert.

The cyanate cyclotrimerization reaction has been employed as a polymer forming reaction.[9] The gradual heating of bulk biscyanates **6** to 250 °C with a zinc chloride catalyst afforded