

# Dynamic Mechanical Properties of Quinazolone-Imide Block Copolymer

AKIRA FUKAMI, KATSUYOSHI IISAKA,\* SHIGERU KUBOTA, and SHOUHEI ETOH

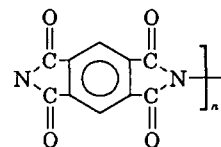
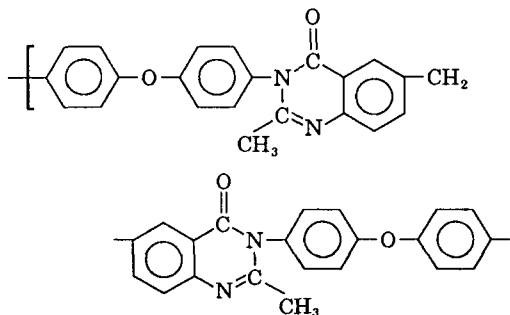
Materials and Electronic Devices Laboratory, Mitsubishi Electric Corporation, Amagasaki Hyougo, Japan

## SYNOPSIS

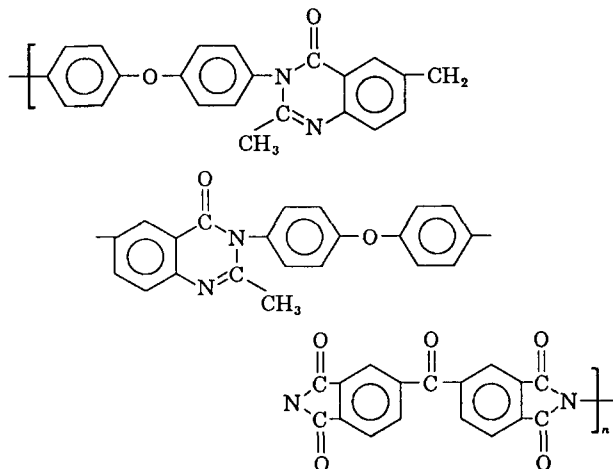
Dynamic mechanical properties have been investigated over the temperature range of  $-150$ – $360^{\circ}\text{C}$  for the quinazolone-imide copolymers, prepared by condensation of the amine-terminated quinazolone prepolymer with a stoichiometric quantity of pyromellitic dianhydride or 3,3',4,4'-benzophenone-tetracarboxylic dianhydride. Both copolymers have, respectively, the low-temperature  $\beta$ -relaxation and the  $\beta^*$ -relaxation, as well as the case of poly(4,4'-oxydiphenylene-pyromellite-imide) (Kapton) examined for comparison. These relaxations seem to contribute to toughness of the copolymers. The  $\alpha$ -relaxations for both copolymers occurred at much the same temperature of  $320^{\circ}\text{C}$ , which can be assigned to a large scale segmental motion of the quinazolone chain sequence. The  $\alpha$ -peak temperatures shifted into higher temperatures by heat aging. This can be explained in terms of crosslinking in the copolymers, supported by swelling test in hot *m*-cresol and IR spectroscopy.

## INTRODUCTION

Aromatic polyimides exhibit excellent heat resistance and toughness over a wide temperature range. However, they are usually insoluble in common solvents. Improvement of the solubility can be done by introduction of aliphatic units as anhydride in the polymer chain, though the heat resistance lowers as a result of the decrease of aromaticity of the polyimide.<sup>1-5</sup> The quinazolone-imide copolymers, which improved the solubility of the polyimide while maintaining thermal stability, were reported as new copolymers, which have the following structures, respectively<sup>6,7</sup>:



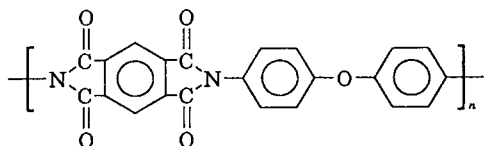
and



The thermal stability evaluated by thermogravimetric analysis was reported to be good for both copolymers.<sup>6,7</sup> Then, the films of them were strong

\* To whom correspondence should be addressed.

and tough as well as poly(4,4'-oxydiphenylene-pyromellitimide) (Kapton) which has the structure



In general, dynamic mechanical measurement provides a fundamental information with regard to mechanical properties of polymers. In this study, dynamic mechanical properties have been examined for both copolymers, compared with Kapton.

## EXPERIMENTAL

### Sample Preparation

Quinazolone-imide copolymers were prepared by a previously reported procedure.<sup>6</sup> The preparation was roughly as follows. Amine-terminated quinazolone prepolymer was prepared by condensation of an equivalent molar ratio of 6,6'-methylenebis(2-methyl-4H,3,1-benzoxazine-4-one) (BOD) with 4,4'-diaminodiphenyl ether in *m*-cresol. BOD was prepared from the reaction of 4,4'-diaminodiphenyl methane-3,3'-dicarboxylic acid with acetic anhydride. The copolymers were prepared by condensation of the amine-terminated quinazolone prepolymer with a stoichiometric quantity of pyromellitic anhydride (PMDA) or 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) in *m*-cresol.

The polymer solution in *m*-cresol was coated onto a tinplate and heated at 100°C for 2 h under atmosphere, followed by at 200°C for 4 h under nitrogen. Then, the polymer film was peeled from the tinplate by an Hg amalgam method and washed with concentrated hydrochloric acid, followed with water. The film was heated under nitrogen at 250°C for 2 h to insure complete imidization. The names of the copolymers were designated as PMDA-QA and BTDA-QA, respectively, in the case of PMDA and BTDA as an anhydride.

The film of poly(4,4'-oxydiphenylene-pyromellitimide) was Kapton H (registered name, E. I. Du Pont de Nemours & Co.).

### Measurements

Dynamic mechanical properties were measured at 3.5 Hz over the temperature range of about -150-360°C by using a Toyo-Baldwin Rheovibron DDV-IIC. A heating rate of samples was about 2°C/min.

Swelling tests were done in *m*-cresol at 25 and 100°C for a virgin specimen and a heat-aged specimen which dynamic mechanical measurement had been completed till about 360°C. IR spectra were also measured for these samples by a KBr method.

## RESULTS AND DISCUSSION

The temperature dependences of dynamic mechanical properties of PMDA-QA, BTDA-QA, and Kapton are shown in Figures 1-3. In the whole temperature range studied here, PMDA-QA and BTDA-QA show evidences for at least four or possibly five relaxations, whereas Kapton shows evidences for possibly three relaxations. Both quinazolone-imide copolymers show the peaks in the loss modulus  $E''$  at roughly the same temperatures, respectively, of -100, 60, 110, 210, and 320°C. On the other hand, Kapton shows the peaks in  $E''$  at the temperatures near -88, 80, and 109°C, and a slow rise above 300°C. The temperature profiles of  $\tan \delta$  or  $E''$  are very similar among both copolymers and Kapton in the temperature range from -150 to about 160°C.

The similarity of the temperature profiles of  $E''$  among these polymers suggests that the molecular mechanisms of the quinazolone-imide copolymers are alike to those of Kapton. The numbers of relaxations or the interpretation of the observed relaxations in terms of polymer structure has been not necessarily made clear for Kapton up to date. However, the lower temperature relaxations, designated  $\beta$  and  $\beta^*$ , respectively, at -88 and 109°C were elucidated at some length in the previous studies.<sup>8-11</sup> That is, it has been concluded that the  $\beta$ -relaxation can be attributed to the presence of water, from the point of view that its strength increases with increase of water content<sup>9</sup> and that the  $\beta$ -relaxation can be associated with combined or coupled motion of the phenylene rings and the nearby O and N atoms.<sup>9,11</sup>

The peak temperature in the  $\beta$ -relaxation of both copolymers is lower by about 10°C than that for Kapton. This relaxation is attributed to motion of residual water molecules that are H-bonded to O atoms of phenylene oxide unit.<sup>9</sup> The mobility of water molecules depends on strength of a hydrogen bonding, which varies by environmental circumstance of phenylene oxide unit. Aromatic polyimide is known to have the structure of molecular aggregation consisting of bundles of parallel-packed main chains.<sup>10-12</sup> Formation of molecular aggregation

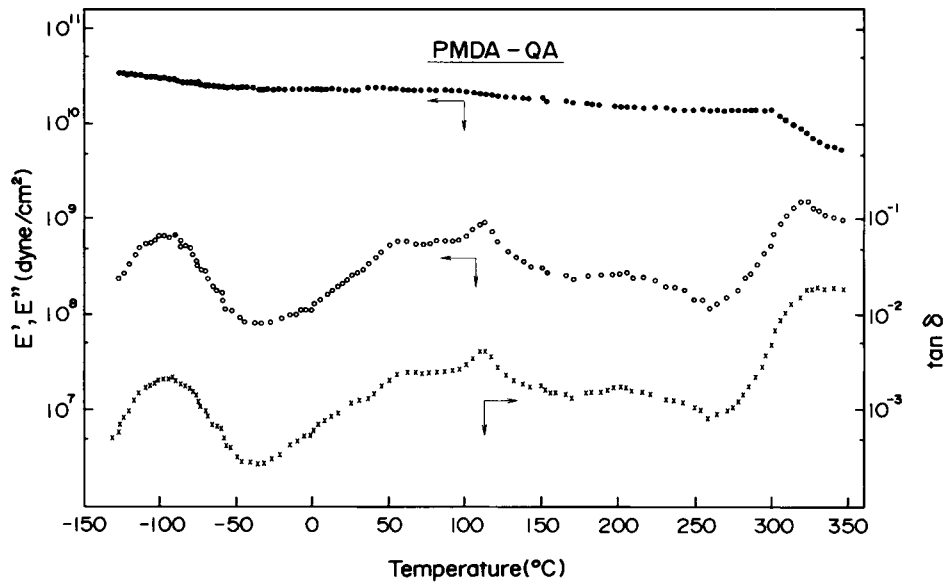


Figure 1 Temperature dependences of dynamic mechanical properties of PMDA-QA.

seems to be due to the rigidity of the chain and the strong interaction between the molecular chains. The introduction of a quinazolone unit into an imide homopolymer can be considered to make looser the packing state of molecular chains in the copolymer, as a result of the decrease in the regularity of the molecular structure and the weakened interaction between the molecular chains. Accordingly, the water molecules on phenylene oxide in the quinazolone-imide copolymer seem to result in formation

of a weaker H-bonding, compared with Kapton. Therefore, the lowering in the peak temperature of both copolymers is considered to be due to a larger mobility of water molecules.

The small peak observed near 80 °C for Kapton had been not detected in the previous studies. This peak may be regarded as a shoulder of 109 °C peak due to the  $\beta^*$ -relaxation. Such a small peak is considered to have appeared as a result of more careful measurement conducted here. In the case of both

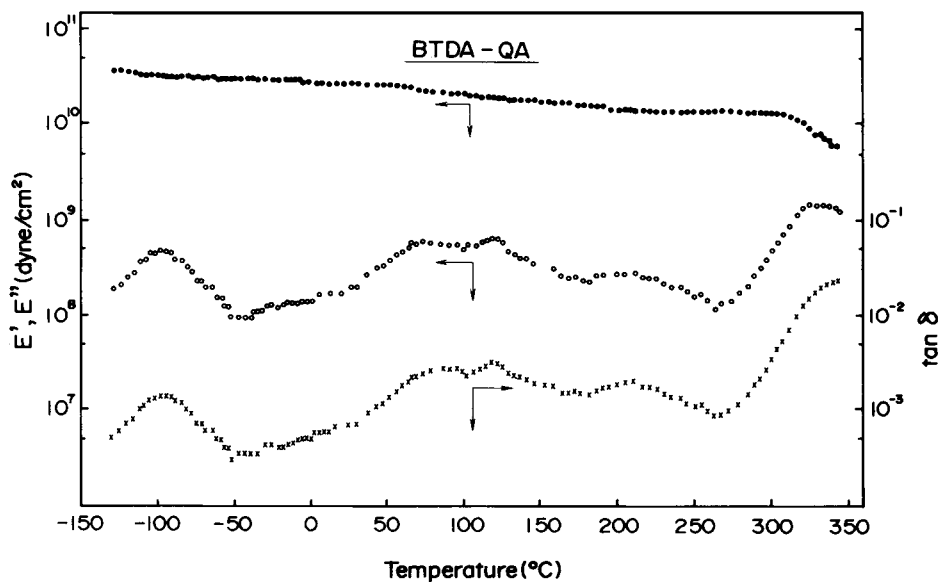


Figure 2 Temperature dependences of dynamic mechanical properties of BTDA-QA.

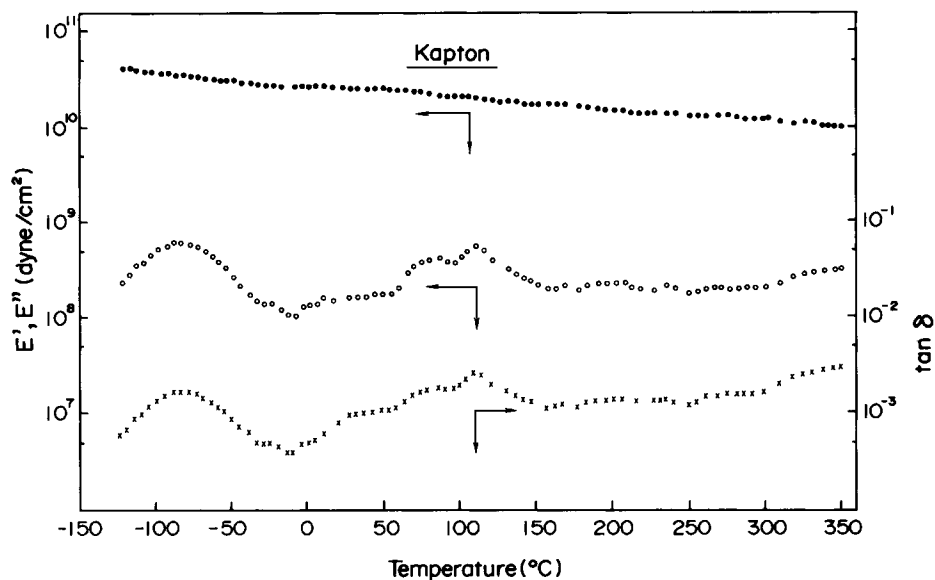


Figure 3 Temperature dependences of dynamic mechanical properties of Kapton.

copolymers, the small peak at near 60°C can be considered to be a shoulder of the  $\beta^*$ -relaxation at 110°C, as well as the case of Kapton. Though it is difficult to make clear the origin of the shoulder in terms of molecular structure, the shoulder may have appeared owing to a discrete distribution in mobility of phenylene unit about N- $\phi$ -O axis. Then, the lower peak temperature of the shoulder in the quinazolone-imide copolymer seems to be due to a more discrete distribution of the motion yielding from a different environmental circumstance of phenylene unit, compared with Kapton.

It is indistinct whether the relaxation near 210°C for the quinazolone-imide copolymer corresponds to the small relaxation near 230°C, designated  $\beta'$  for Kapton, though not observed here. The  $\beta'$ -mechanism has been concluded to be attributed to a torsional oscillation mode of unit containing pyromellite imide connected by phenylene oxide which is a longer range motion than the  $\beta^*$ -relaxation. Accordingly, the relaxations at near 210°C for the copolymers may be attributed to a torsional oscillation mode of unit containing quinazolone molecule and/or pyromellite imide, connected by phenylene oxide.

Both copolymers show the  $\alpha$ -peaks in  $E''$  at nearly the same temperature of about 320°C. In the corresponding temperature regions, the storage modulus  $E'$  shows a relatively large decrease. In Figure 3, Kapton shows a small but steady increasing behavior in loss at above near 300°C. A peak in  $E''$  corresponding to  $\alpha$ -dispersion was reported near 420°C for Kapton.<sup>9-11</sup> The  $\alpha$ -peak was very broad

and the decrease in the storage modulus was very small. The mode of molecular motion corresponding to the  $\alpha$ -dispersion has been concluded to be a long-range cooperative motion of the main chain which is associated with the glass transition. The increasing loss above near 300°C in Figure 3 is probably associated with the beginning of the  $\alpha$ -relaxation.

The  $T_g$  of polyimides is lowered by a reduction of the interchain interactions rather than by a decrease in rigidity of the chain through the introduction of flexibilizing linkages.<sup>13</sup> The interchain interactions in polyimides are charge transfer complexes whose strength is dependent on the electron affinity of the dianhydride and the ionization potential of the diamine.<sup>13</sup> The  $T_g$  of the quinazolone-imide copolymer is expected to become lower than that of Kapton, since the quinazolone unit has a lower electron affinity than pyromellite dianhydride. Accordingly, the  $\alpha$ -dispersion observed at about 320°C for the copolymer seems to be attributed to a large scale backbone chain motion, corresponding to the glass transition.

Benzophenone tetracarboxylic dianhydride in BTDA-QA has a lower electron affinity and a more flexible linkage than pyromellite dianhydride in PMDA-QA. Therefore, the  $T_g$  of BTDA-QA can be predicted to become lower than that of PMDA-QA. However, both copolymers have much the same  $\alpha$ -peak temperature of about 320°C. This seems to mean that the  $\alpha$ -relaxation is not attributed to a segmental motion of the random chain sequences of the quinazolone and the imide groups, but a large

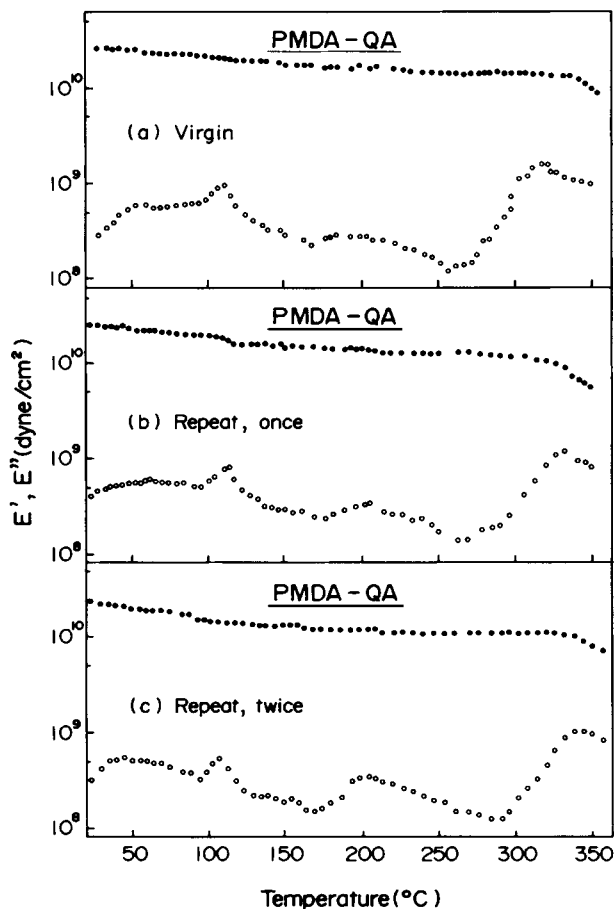


Figure 4 Effect of heat aging on temperature dependences of dynamic mechanical properties of PMDA-QA.

scale chain motion originated in a similar molecular structure unit, that is, a large scale motion of quinazolone chain sequences in the quinazolone-imide block copolymer.

However, in the case of the quinazolone-imide copolymer, it should be taken into consideration that the decrease in  $E'$  and the increase in  $\tan \delta$  above  $300^\circ\text{C}$  may be associated with degradation of the samples. The specimens for which dynamic mechanical measurements had been done, changed from light brown in a virgin specimen to dark brown. If degradation occurs considerably in the sample, the sample will have a lower  $T_g$  than the virgin sample. Thus, dynamic mechanical measurements were repeatedly done for the same specimen.

Figures 4-6 show the results of repeat measurements on dynamic mechanical properties for PMDA-QA, BTDA-QA, and Kapton, respectively. The repeat measurements manifested no changes on the peak temperature and strength in the  $\beta$ - and  $\beta^*$ -dispersions below about  $160^\circ\text{C}$  for any polymers,

though the data below  $0^\circ\text{C}$  were not cited in those figures. However, the repeat measurements changed the dynamic mechanical properties at the temperature regions above  $160^\circ\text{C}$  for both copolymers, whereas it did not change for Kapton. Especially, the peak temperature shifted into a higher temperature and the decrease in the storage modulus became small in the  $\alpha$ -dispersion temperature regions. The shift in  $T_g$  was about  $30^\circ\text{C}$  for PMDA-QA and over  $40^\circ\text{C}$  for BTDA-QA in the case of twice repeat measurements. Unfortunately, it was difficult to measure dynamic mechanical properties at the temperatures above  $360^\circ\text{C}$  on account of a marginal capacity of the present instrument. Such increase in  $T_g$  by heat aging suggests that crosslinking occurs rather than degradation in the polymer chains. On the other hand, the  $\beta'$ -dispersion became clearer with shift into a higher temperature of the  $\alpha$ -peak temperature, though the  $\beta'$ -peak temperature did not change. This seems to have resulted from liberation of the  $\beta'$ -relaxation from the overlapped  $\alpha$ -relaxation.

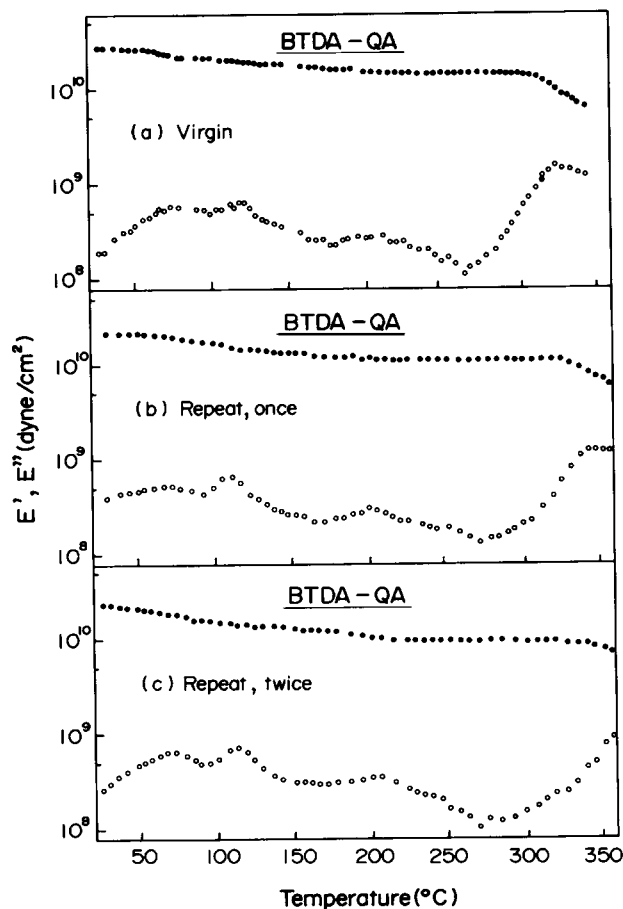
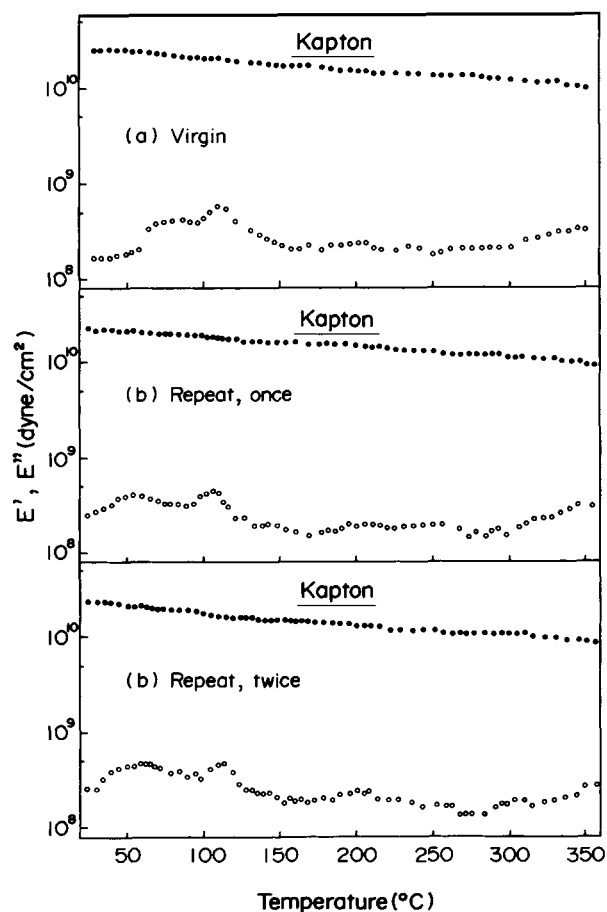


Figure 5 Effect of heat aging on temperature dependences of dynamic mechanical properties of BTDA-QA.



**Figure 6** Effect of heat aging on temperature dependences of dynamic mechanical properties of Kapton.

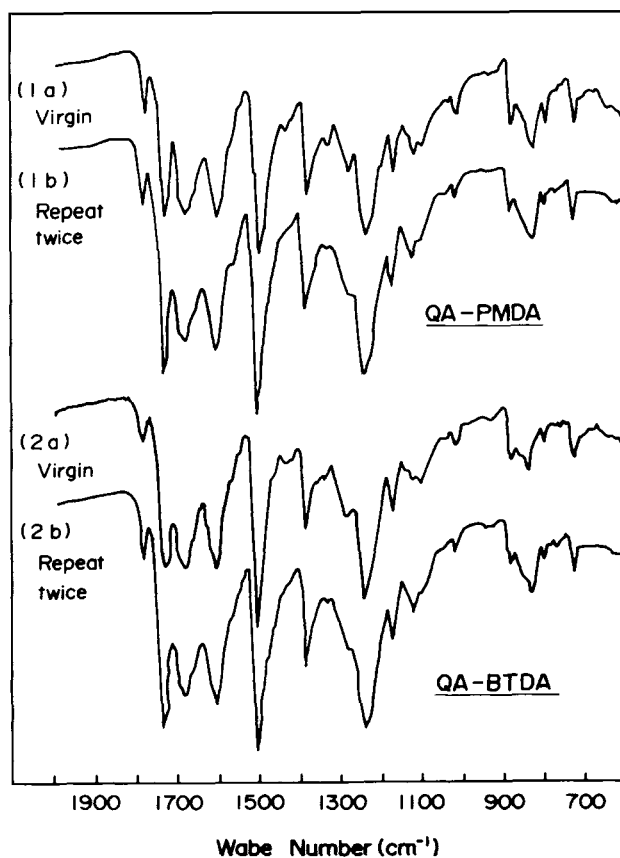
Thus, a swelling experiment was done in *m*-cresol in order to obtain an evidence of crosslinking. Table I lists the degree of swelling for both quinazolone-imide copolymers. Slight weight losses in both samples were observed under an immersing condition of 50 h at 25°C, indicating that low molecular-weight materials were extracted. When specimens were immersed under a condition of 2 h at 100°C, the virgin samples broke to pieces in the case of PMDA-QA and expanded in size in the case of BTDA-QA. The virgin samples absorbed a large amount of *m*-cresol and the degree of swelling were 26 and 48% for QA-PMDA and QA-BTDA, respectively. However, for the heat-aged samples, the degree of swelling were very small even under the immersing condition of 2 h at 100°C. These results support that crosslinking occurs in the quinazolone-imide copolymers by heat aging.

Figure 7 shows the IR spectra of the virgin and heat-aged samples for both copolymers. By heat aging, the intensities of the absorption bands at 1680

**Table I** Degree of Swelling of the Quinazolone-Imide Copolymers in *m*-Cresol

Sample	Degree of Swelling (%)	
	20°C × 50 h	100°C × 2 h
PMDA-QA		
Virgin	-1.1	+26
After once repeating measurement	-1.3	+0.7
After twice repeating measurement	-2.8	-0.6
BTDA-QA		
Virgin	-1.2	+48
After repeating measurement	-2.3	-0.8
After twice repeating measurement	-3.6	0

and 1590  $\text{cm}^{-1}$  due to quinazolone ring decreased, whereas the intensities of the absorption bands at 1776, 1720, 1380, and 723  $\text{cm}^{-1}$  due to imide group



**Figure 7** IR spectra of the virgin and heat aged samples of PMDA-QA and BTDA-QA.

**Table II** Change of the Ratios of the Absorption Bands at 1776 and 1680  $\text{cm}^{-1}$  Due to the Imide and Quinazolone Rings, Respectively, to the Standard Absorption Band at 1012  $\text{cm}^{-1}$

Sample	$\nu_{1776}/\nu_{1012}$	$\nu_{1680}/\nu_{1012}$
PMDA-QA		
Virgin	2.5	3.8
After twice repeating measurement	2.4	2.8
BTDA-QA		
Virgin	1.6	3.6
After twice repeating measurement	1.6	2.9

scarcely varied. Then, the intensity ratios of  $\nu_{1776}$  and  $\nu_{1680}$  to  $\nu_{1012}$  as a reference aromatic absorption<sup>14</sup> were examined to evaluate the changes of quinazolone and imide rings, respectively. The quinazolone portion suffers some thermal degradation, as listed in Table II. Though it is difficult at the present time to guess into what structures the quinazolone ring changes, the degraded quinazolone ring seems to take part in crosslinking in the interchains of the copolymers.

In conclusion, the quinazolone-imide copolymers have several mechanical dispersions due to the local mode motions below the temperature of the  $\alpha$ -dispersion corresponding to the glass transition. It was reported by many investigators that low temperature relaxations in polymers are generally associated with toughness of the polymers.<sup>15,16</sup> Especially, the mechanical relaxation which is observed near room temperature is more effective in increasing toughness of polymers.<sup>17</sup> The present  $\beta$ - and  $\beta^*$ -relaxations observed in the copolymers as well as Kapton seem to contribute to the toughness of these polymers. The  $\alpha$ -relaxations of both copolymers, PMDA-QA and BTDA-QA, occurred at roughly the same temperature of about 320°C. The  $\alpha$ -relaxation seems to be associated with the segmental motion of the quinazolone chain sequence, indicating that

the polymers are the block copolymers of quinazolone and imide chains. In the case of both copolymers, the repeat measurements of the same specimens on dynamic mechanical properties allowed to shift the  $\alpha$ -peak temperature into a higher temperature. It is concluded that the quinazolone-imide copolymers suffer crosslinking by heat aging.

## REFERENCES

1. Y. Iwakura, C. P. Yang, and K. Uno, *Macromol. Chem.*, **175**, 137 (1974).
2. F. Nakanishi, H. Hasegawa, and H. Takahashi, *Polymer*, **14**, 440 (1973).
3. J. P. Critchley, P. A. Grattan, M. A. White, and J. S. Pippet, *J. Polym. Sci. A-1*, **10**, 1789 (1972).
4. M. M. Koton, *Polym. Sci. USSR*, **A13**, 1513 (1971).
5. M. Dror and M. Levy, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 171 (1975).
6. A. Fukami, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 1535 (1977).
7. S. Nishizaki and A. Fukami, *Koubunshi Ronbunshuu*, **32**(7), 445 (1975).
8. E. Butta, S. De. Petris, and M. Pasquini, *J. Appl. Polym. Sci.*, **13**, 1073 (1969).
9. T. Lim, V. Frosini, V. Zaleckas, D. Morrow, and J. A. Sauer, *Polym. Eng. Sci.*, **13**(1), 51 (1973).
10. S. Isoda, M. Kochi, and H. Kambe, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 837 (1982).
11. M. Kochi, H. Shimada, and H. Kambe, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 1979 (1984).
12. S. Isoda, H. Shimada, and H. Kambe, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1293 (1981).
13. M. Fryd, *Polyimide* Plenum, New York/London, 1984, Vol. 1, p. 377.
14. R. Ginsberg and J. R. Susko, *Polyimide* Plenum, New York/London, 1984, Vol. 1, p. 237.
15. Y. Wada and K. Kasahara, *J. Appl. Polym. Sci.*, **11**, 1661 (1967).
16. E. Sacher, *J. Appl. Polym. Sci.*, **19**, 1421 (1975).
17. M. Ochi, Z. Shouen, and M. Shimbo, *Polymer*, **27**, 1569 (1986).

Received October 2, 1990

Accepted November 9, 1990