Properties of Copolyimides Prepared from Different Tetracarboxylic Dianhydrides and Diamines

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SYNOPSIS

Various copolyimides were prepared from two acid dianhydrides (BPDA, 3,3',4,4'-biphenyl tetracarboxylic dianhydride; PMDA, pyromelitic dianhydride) and two diamines (PPD, *p*-phenylene diamine; ODA, 4,4'-oxydianiline). The thermal and mechanical properties of these polyimides were examined in detail. By appropriately selecting the ratios of the acid dianhydride component and the diamine component, polyimide films having desirable mechanical and thermal characteristics can be obtained. Further, it was proved that there is a correlation between the properties and the compositions of the copolyimides and that the properties could be estimated from the compositions by the use of multiple regression analysis. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have been widely used in the electric and electronic industries for high chemical and heat resistance and superior mechanical and electrical properties. However, in order to achieve a combination of desired properties, such as low thermal expansion coefficient (TEC), high modulus of elasticity, and high glass transition temperature (T_g), in one polymer system, copolymerizations are utilized, or the incorporation of fluorine in polyimides has been studied. However, the fluorinated aromatic acid dianhydrides and diamines used in these studies are special monomers and are very expensive.[1-4] We considered that the copolyimides prepared from two acid anhydrides (BPDA, 3,3',4,4'-biphenyl tetracarboxylic dianhydride; PMDA, pyromelitic dianhydride) and two diamines (PPD, *p*-phenylene diamine; ODA, 4,4'-oxydianiline) seemed to be most probable. The structures of the two acid dianhydrides and two diamines are shown in Figure 1. The properties of the copolyimides from BPDA/PMDA-PPD/ODA have not been studied so far.[5-9]

In this work, we report that the desired properties are obtained by combinations of the two acid anhydrides (BPDA and PMDA) and two diamines (PPD and ODA).[10]

EXPERIMENTAL

Samples

The polyamic acid used in this study was prepared in *N*-methyl-2-pyrrolidone by polymerizing substantially equimolar amounts of an aromatic tetracarboxylic acid component composed of BPDA and PMDA and an aromatic diamine component composed of PPD and ODA. The obtained aromatic polyamic acid solution was cast with a thickness of about 150 μm on a copper foil having a thickness of about 30 μm. The solution film was dried and solidified by elevating the temperature from 60 to 200°C and was finally treated by elevating the temperature to 350 or 400°C. A copper-clad laminate composed of an aromatic polyimide film layer having a thickness of 35 μm was obtained. The copper film layer was dissolved away by an etching solution of ferric chloride to obtain an aromatic polyimide film.

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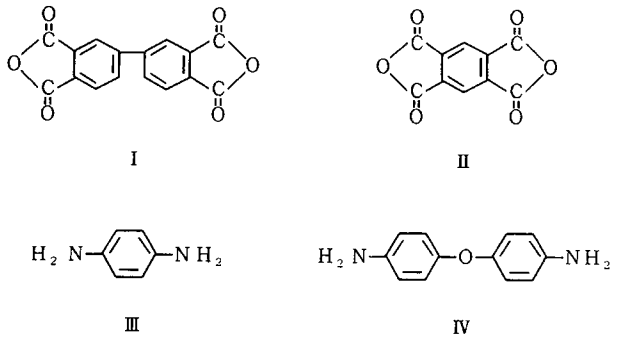

I II

III IV

Figure 1 Structure of monomers. (I) BPDA, (II) PMDA, (III) PPD, (IV) ODA.

Analysis

Tensile properties were obtained according to the ASTM method D882-67 with a Shimadzu Autograph IM-100. The thermomechanical analyses (TMA) were performed with a Rigaku CN 8098A1 Thermomechanical Analyzer. A film of 5 mm in width and 10 mm in length (between chucks) was used as a sample. The sample was placed and heated to 450°C to get rid of residual stress. After cooling to room temperature, the TEC and the T_g were determined by the TMA tensile method. The TEC at a temperature ranging from 100 to 300°C (or from 100 to 250°C) was measured at a heating rate of 10°C/min under a load of 2 g. T_g was measured at a heating rate of 10°C/min under a load of 10*g*.

RESULTS AND DISCUSSION

Copolyimides from Three Component Systems

The properties of the homopolyimides and the copolyimides from three component systems are shown in Table I. The polyimide from BPDA-PPD has the highest modulus, the highest T_g, and the lowest TEC among the polyimides from BPDA-PPD/ODA. These properties may be attributed to the rigid structure of BPDA and PPD[11] because of the nonflexible linkage in the backbone structure. On the other hand, ODA has a flexible ether linkage because bending and rotation of the molecular chain are possible. As the fraction of PPD decreases, the modulus and T_g decrease (Figs. 2 and 3). On the other hand, TEC increases with a decrease of the PPD fraction. Numata et al.[11] reported the same results on TEC that we obtained. Both the modulus and the TEC change gradually with a decrease of the PPD fraction, but the change of T_g is fairly large. The T_g of the polyimide from BPDA-PPD is 420°C, while that of PPD/ODA (9/1) is 330°C. Even if the small proportion of ODA having a flexible linkage is incorporated with the chain structure, the structure is disturbed and the large drop of T_g occurs. This result shows that the simple additivity of component contribution would fail with respect to T_g and that the effect of component would be sensible for rigidity. Han et al.[9] studied the blends of the polyamic acid in BPDA-PPD and PMDA-ODA

Table I Properties of Homopolyimides and Copolyimides from Three Component Systems

Monomers (mol %)				Elongation at Break (%)	Modulus of Elasticity (GPa)	TEC ($\times 10^{-6}$ K^{-1})	T_g (°C)
BPDA	PMDA	PPD	ODA				
100	0	100	0	48	7.7	14	420
100	0	90	10	41	6.9	15	330
100	0	80	20	59	6.1	17	320
100	0	70	30	71	5.7	21	310
100	0	60	40	52	5.4	32	300
100	0	50	50	64	4.5	36	290
100	0	0	100	100	3.8	40	285
80	20	100	0	56	7.9	14	335
80	20	0	100	84	2.9	35	292
70	30	100	0	49	7.7	14	357
70	30	0	100	77	2.8	36	294
60	40	100	0	46	6.8	13	384
50	50	100	0	38	6.4	14	369
50	50	0	100	74	2.7	41	305
0	100	100	0	Brittle			
0	100	50	50	19	3.6	33	370
0	100	0	100	86	2.8	31	373

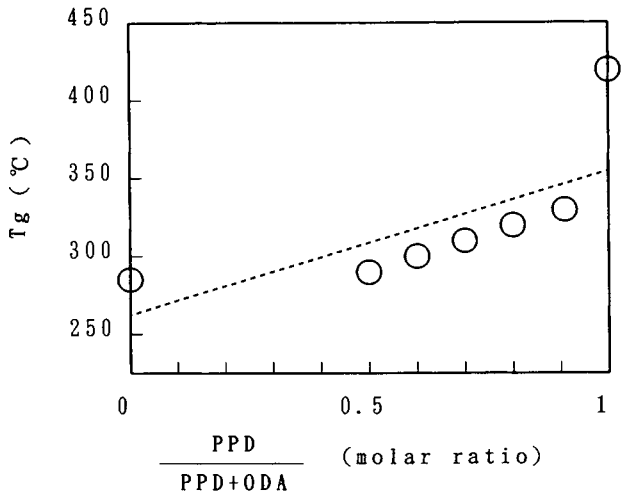

Figure 2 T_g of copolyimides from BPDA-PPD/ODA. Open circle, experimental data; dashed line, estimate.

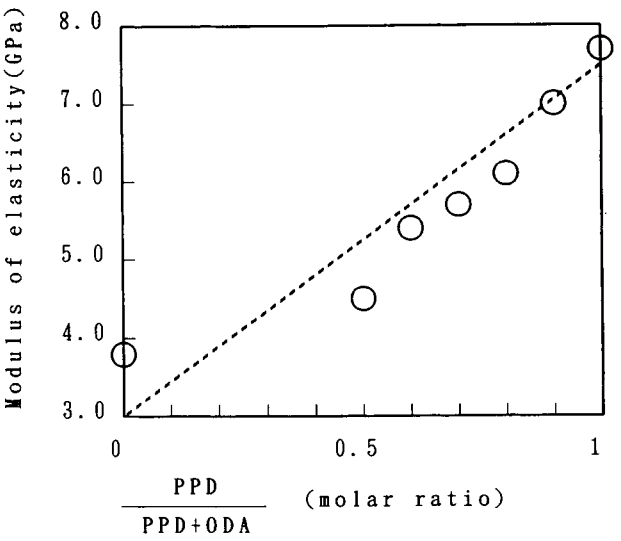

Figure 3 Modulus of elasticity of copolyimides from BPDA-PPD/ODA. Open circle, experimental data; dashed line, estimate.

combinations and found that these blends showed lower T_g than those expected from either polyimide alone. They insisted that the T_g should be explained in terms of intermolecular characteristics, such as molecular packing, rather than the change in the polymer backbone.

The polyimide film from PMDA-PPD was expected to have the highest modulus and T_g among the above systems. However, unfortunately, we obtained only very brittle film. Even the copolyimide from PMDA-PPD/ODA (50/50) has only 19% elongation. The TEC of this copolyimide is 33×10^{-6} K^{-1}. The polyimide from PMDA-ODA has a large TEC. Nagano et al.[12] studied copolyimides from PMDA-PPD/ODA and obtained the same results that we did with regard to random copolyimides. In addition, they reported that the copolyimides prepared by sequence-controlled copolymerization have larger elongation and lower TEC than the values obtained by random copolymerization. Oishi et al.[13] and Yamamoto et al.[14] reported that the modulus and T_g increased with PPD content in the copolyimides. Oishi et al.[13] also pointed out that any clear difference between random and block copolyimides was not observed, but they did not mention elongation.

Copolyimides from BPDA/PMDA-PPD or BPDA/PMDA-ODA were examined next. The copolyimides prepared from BPDA/PMDA-PPD have large elongation and a high modulus, when the BPDA fraction is larger than 50 mol % and the TEC values of the copolyimides are less than 15×10^{-6} K^{-1}. On the other hand, the copolyimides from BPDA/PMDA-ODA have a TEC larger than 30×10^{-6} K^{-1} (Fig. 4) and larger elongation than that of BPDA/PMDA-PPD.

Multiple Regression Analysis of Copolyimides from Homopolyimides and Three Component Systems

We tried to estimate the properties of the copolyimides by multiple regression analysis using the results of the homopolyimides and the copolyimides in three

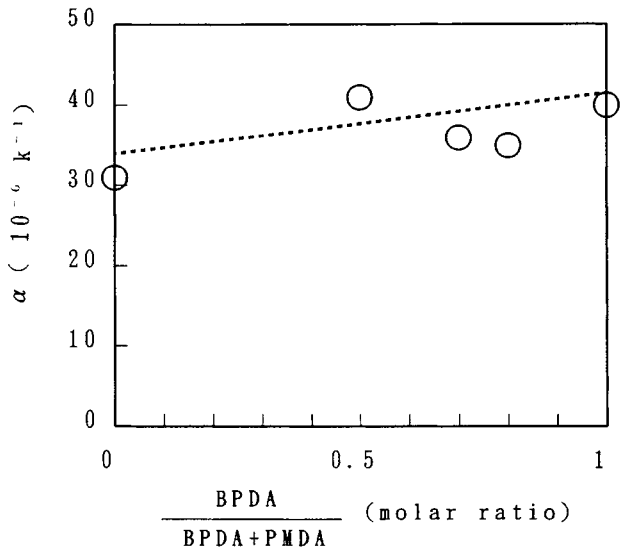

Figure 4 Thermal expansion coefficient (α) of copolyimides from BPDA/PMDA-ODA. Open circle, experimental data; dashed line, estimate.

Table II Properties Estimated by Using Results of Homopolyimides and Copolyimides in Three Component Systems

Monomers (mol %)				Elongation at Break (%)	Modulus of Elasticity (GPa)	TEC ($\times 10^{-6}$ K^{-1})	T_g (°C)
BPDA	PMDA	PPD	ODA				
100	0	0	100	87	3.0	42	262
100	0	100	0	52	7.5	14	354
0	100	0	100	71	2.5	34	368
0	100	100	0	13	5.8	20	381

component systems. If a linear relationship exists between the properties and the monomer compositions, then the estimates of the properties could be obtained from monomer compositions by multiple regression analysis. The copolyimides prepared are random copolyimides in this analysis, but we assumed that the properties of the copolyimides could be explained by mole fractions of the homopolyimides. Then, mole fractions of each homopolyimide component can be calculated from the molar ratios of four monomers. In the case of BPDA/PMDA (7/3)-PPD/ODA (7/3), the mole fractions of the homopolyimides of BPDA-PPD, BPDA-ODA, PMDA-PPD, and PMDA-ODA are 0.49, 0.21, 0.21, and 0.09, respectively. These molar fractions of each homopolyimide are used as explanatory variables in multiple regression analysis. The linear multiple regression equations of elongation at break, modulus of elasticity, TEC, and T_g, respectively, can be obtained.

$$\hat{y} = \hat{a}_0 + \hat{b}_1 S + \hat{b}_2 T + \hat{b}_3 U + \hat{b}_4 V \qquad (1)$$

Here, $\hat{y}$ is the estimate of the criterion variable, such as elongation at break, modulus of elasticity, TEC, and T_g. $\hat{a}_0$ is the estimate of the constant term. $\hat{b}_1$, $\hat{b}_2$, $\hat{b}_3$, and $\hat{b}_4$ are the estimates of the partial regres-

Table III Properties of Copolyimides from BPDA/PMDA-PPD/ODA

Monomers (mol %)				Elongation at Break (%)	Modulus of Elasticity (GPa)	TEC ($\times 10^{-6}$ K^{-1})	T_g (°C)
BPDA	PMDA	PPD	ODA				
90	10	50	50	46	4.2	37	290
80	20	90	10	40	6.5	22	310
80	20	80	20	60	5.7	28	308
70	30	90	10	35	6.6	16	315
70	30	80	20	48	5.8	22	322
70	30	70	30	62	4.9	29	315
70	30	60	40	52	4.8	29	320
60	40	90	10	30	5.6	15	393
60	40	80	20	46	5.6	21	348
60	40	70	30	52	4.6	26	340
50	50	80	20	40	5.7	21	350
50	50	70	30	60	5.0	19	360
50	50	60	40	60	4.4	28	347
40	60	70	30	44	4.8	19	407
40	60	60	40	44	4.7	21	350
40	60	50	50	59	3.8	26	357
30	70	90	10	20	5.0	13	410
30	70	70	30	58	4.6	25	400
30	70	50	50	42	3.6	21	360
30	70	20	80	68	2.9	42	335
20	80	70	30	26	4.7	18	396
20	80	50	50	40	3.8	26	403
10	90	90	10	10	4.7	7	430

Table IV Properties of Homopolyimides Estimated by Using Results of Copolyimides in Four Component Systems

Monomers (mol %)				Elongation at Break (%)	Modulus of Elasticity (GPa)	TEC ($\times 10^{-6}$ K^{-1})	T_g (°C)
BPDA	PMDA	PPD	ODA				
100	0	0	100	68	0.7	56	259
100	0	100	0	57	7.7	22	281
0	100	0	100	90	2.8	42	350
0	100	100	0	1	4.9	1	477

sion coefficient. S, T, U, and V are mole fractions of the homopolyimides of BPDA-PPD, BPDA-ODA, PMDA-PPD, and PMDA-ODA, respectively. The coefficient of determination (R^2) of the obtained multiple regression equations for elongation at break, modulus of elasticity, TEC, and T_g are 0.72, 0.94, 0.86, and 0.70, respectively. The modulus of elasticity shows a good correlation, but the elongation at break and T_g show a bad correlation among them. This low coefficient of determination (R^2) of elongation is thought to occur because the reproducibility of the data is not good. The low R^2 of T_g is thought to be due to the remarkably high T_g of the polyimide of BPDA-PPD. The estimates of the properties of the homopolyimides are shown in Table II. With regard to the homopolyimides of BPDA-ODA, BPDA-PPD, and PMDA-ODA, the estimates are not very different from the experimental data, except for the T_g of BPDA-PPD. The estimates of the properties of PMDA-PPD would be different from the expected values, although the properties of its polyimide film are not known because of its brittleness. Both its modulus and its T_g would be more than the estimates, and both its TEC and its elongation at break would be less than the estimates. These estimates are mainly derived from the results of the copolyimides in the three component systems. Because the orientation and crystallinity in the homopolyimide are disordered in the copolyimide, the contribution of the components of the homopolyimide to the properties of the copolyimide is naturally different from that of the homopolyimide itself.

The multiple regression lines of the copolyimides prepared from the three component systems are shown by dashed lines in Figures 2–4. With regard to T_g in Figure 2, the multiple regression line is approximately in accordance with the experimental data except for BPDA-PPD. There are the same correlations in Figures 3 and 4. The properties of the copolyimides in the three component systems could be estimated from the compositions by the use of multiple regression analysis.

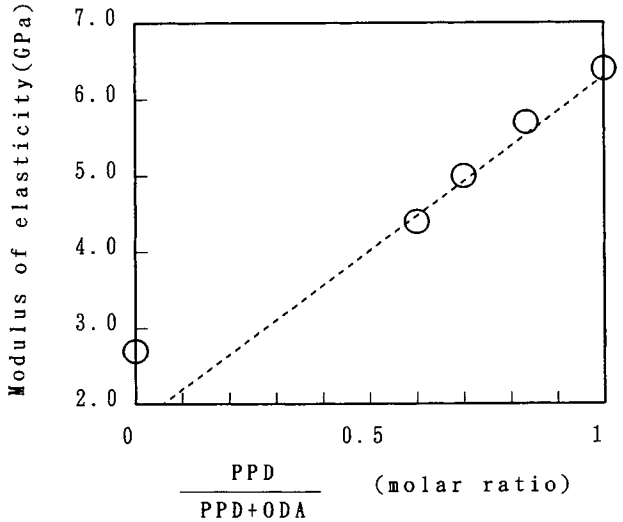

Figure 5 Modulus of elasticity of copolyimides from BPDA/PMDA (50/50)-PPD/ODA. Open circle, experimental data; dashed line, estimate.

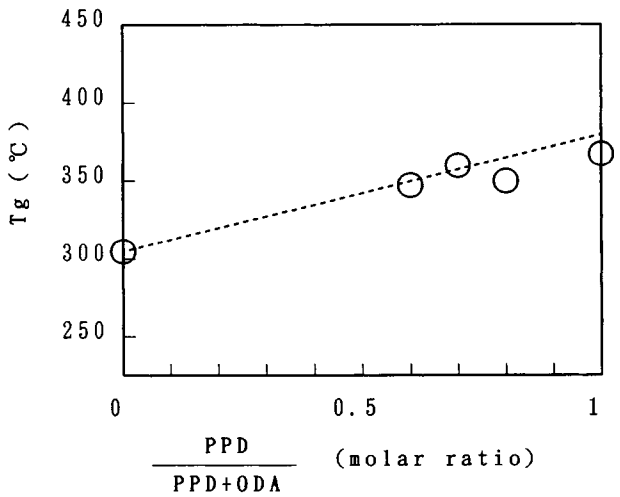

Figure 6 T_g of copolyimides from BPDA/PMDA (50/50)-PPD/ODA. Open circle, experimental data; dashed line, estimate.

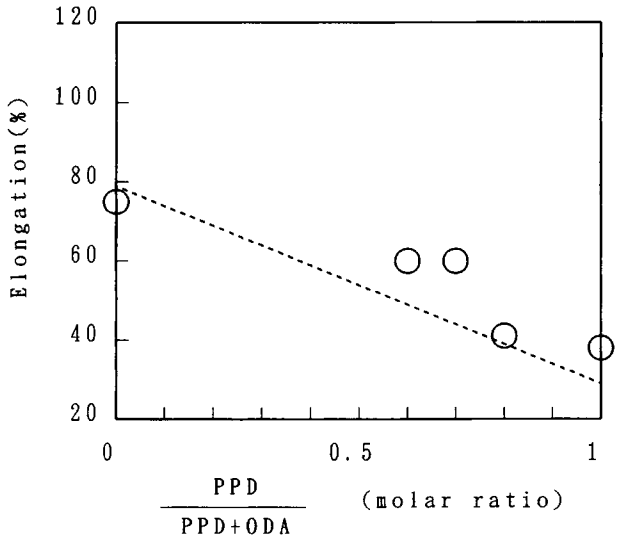

Figure 7 Elongation at break of copolyimides from BPDA/PMDA (50/50)-PPD/ODA. Open circle, experimental data; dashed line, estimate.

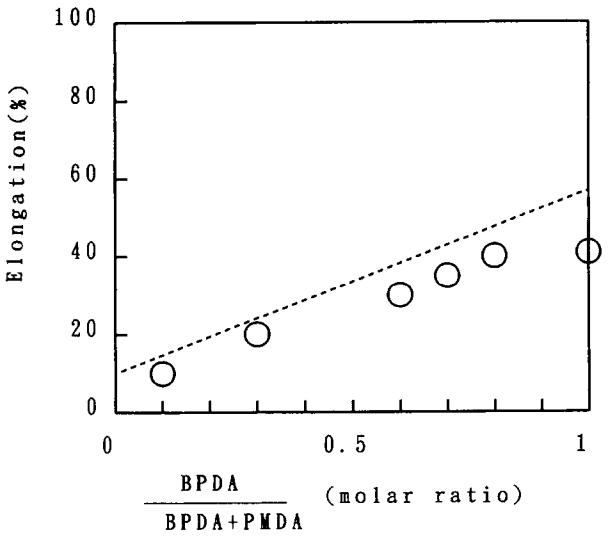

Figure 9 Elongation of BPDA/PMDA-PPD/ODA (90/10). Open circle, experimental data; dashed line, estimate.

Copolyimides Prepared from Four Component Systems

The properties of the copolyimides prepared from the four component systems are shown in Table III. In order to know the correlation between the properties and the compositions, we again estimated the properties of the copolyimides by multiple regression analysis. In this analysis, the data of the four component systems in Table III were used. The coefficient of determination (R^2) of the obtained multiple regression equations for elongation at break, modulus of elasticity, TEC, and T_g are 0.60, 0.93, 0.87, and 0.86, respectively. These results show a tendency similar to the results obtained only from the data of Table I. The R^2 of elongation is also low, but that of T_g is not low. This is thought to occur because there is no polyimide with extremely high or low T_g in the four component systems. The estimates of

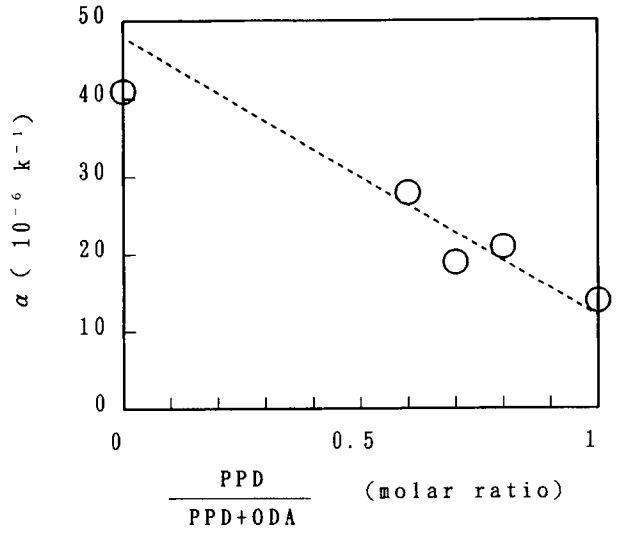

Figure 8 Thermal expansion coefficient (α) of copolyimides from BPDA/PMDA (50/50)-PPD/ODA. Open circle, experimental data; dashed line, the estimate.

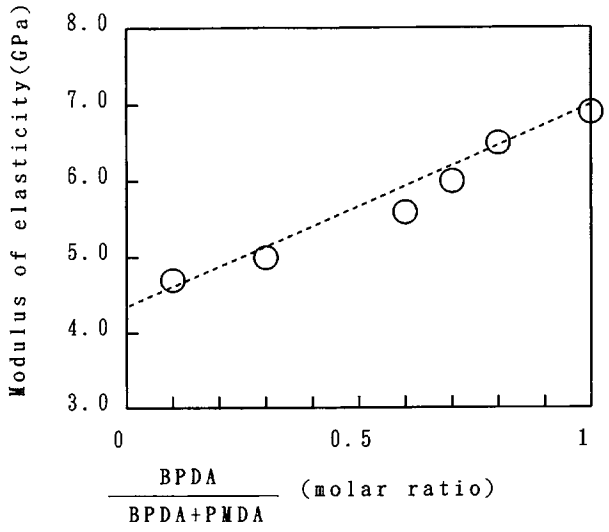

Figure 10 Modulus of BPDA/PMDA-PPD/ODA (90/10). Open circle, experimental data; dashed line, estimate.

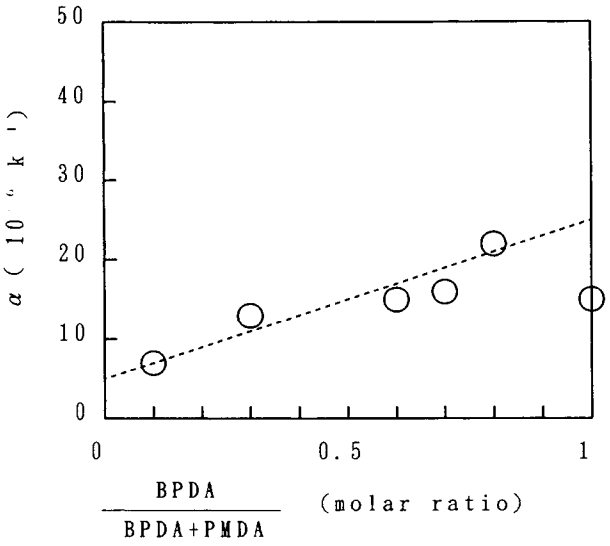

Figure 11 Thermal expansion coefficient (α) of BPDA/PMDA – PPD/ODA (90/10). Open circle, experimental data; dashed line, estimate.

the properties of the homopolyimides are shown in Table IV. There are large differences between the experimental data and the estimates with regard to the homopolyimides of BPDA-ODA and BPDA-PPD. These results also show that the contribution of the components of the homopolyimide to the properties of the copolyimides is different from that of the homopolyimide itself. The properties of the homopolyimide from PMDA-PPD would be close to the expected values except for the modulus of elasticity. The contribution of the components of PMDA-PPD to the properties of the copolyimides is large compared with other components with regard to elongation at break, TEC, and T_g. The correlations between the experimental data and the estimates with regard to the copolyimides prepared from BPDA/PMDA (50/50)-PPD/ODA are shown in Figures 5–8. The estimates are shown by dashed lines. These copolyimides have tendencies similar to those of the BPDA-PPD/ODA system relating to the modulus of elasticity and T_g. Thus, the modulus of elasticity and T_g increase with an increase of the PPD fraction, as shown in Figures 5 and 6. The correlations between the experimental data and the estimates with regard to the copolyimides prepared from BPDA/PMDA-PPD/ODA (90/10) are shown in Figures 9–12. Elongation, the modulus of elasticity, and TEC increase with an increase of the BPDA fraction. Elongation and the modulus of elasticity are thought to be contrary to each other; consequently, it is interesting that both increase with an increase of the BPDA fraction. T_g, on the contrary, decreases with an increase of the BPDA fraction.

With regard to the properties of the copolyimides from BPDA/PMDA-PPD/ODA, there are good correlations between the experimental data and the estimates of the multiple regression analysis. These results demonstrate the additivity of the component contribution in copolyimides from BPDA/PMDA-PPD/ODA. The orientation, crystallinity, and packing in the homopolyimides, such as BPDA/PPD, PMDA/ODA and PMDA/PPD, are disordered in the copolyimide. Then, the additivity could apply in the copolyimides and their properties could be estimated by the use of multiple regression analysis.

CONCLUSIONS

Various copolyimides were prepared from two acid dianhydrides (BPDA and PMDA) and two diamines (PPD and ODA). The thermal and mechanical properties of these polyimides were examined in detail. By appropriately selecting the ratios of the acid dianhydride component and the diamine component, polyimide films having desirable mechanical and thermal characteristics can be obtained. Further, it was proved that there are correlations between the properties and the compositions of the copolyimides and that the properties could be estimated from the compositions by the use of multiple regression analysis.

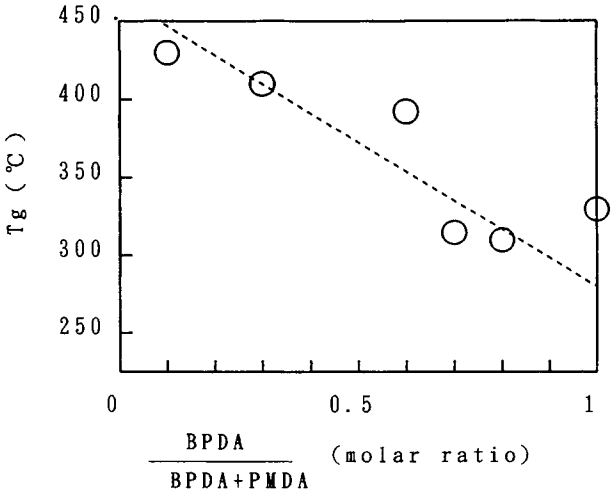

Figure 12 T_g of BPDA/PMDA-PPD/ODA (90/10). Open circle, experimental data; dashed line, estimate.

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