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MECHANICAL AND THERMAL PROPERTIES OF AROMATIC COPOLYESTERS
CONTAINING RIGID BINAPHTHYL UNITS

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ABSTRACT

Mechanical and thermal properties of terephthalic acid copolyesters of 4,4'-binaphthol-1,N monomer and 2,2-bis(4-hydroxyphenyl)propane, A monomer (Bisphenol A), have been examined by differential scanning calorimetry (DSC) and dynamic mechanical methods. The copolyesters had different amounts and sequence distributions of diphenolic units. When the content of N units in the copolyesters was increased from 27 to 55% a significant increase of the dynamic Young's modulus, from 2485 to 4540 MPa at 110 Hz and room temperature, and an enhancement of the stress at yield, from 53.5 to 66.5 MPa, were observed. In the glass transition region of the copolyesters a smaller decrease in the value of E' was noted compared with the homopolymers. For the copolyesters containing 55% of N units, the E' decrease was only about 1.6 decades at 110 Hz within a range of temperatures of over 74°K. The DSC measurements of the copolyesters under consideration showed that the T_g depended only to a slight extent on their composition and structure and all T_g values were within the range of $494 \pm 2^\circ\text{K}$, corresponding to that for poly[2,2-bis(4-hydroxyphenyl)propane terephthalate], the homopolymer of the N bisphenol monomer.

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INTRODUCTION

Terephthalic acid polyesters and copolyesters are well known and widely used for many applications, including compositions based on either aliphatic or cycloaliphatic glycols or aromatic diphenols. Jedlinks, Sek and coworkers investigated the synthesis and properties of fully aromatic homo- and copolyesters, some of which were based on terephthalic acid and a mixture of bisphenols and binaphthols and these showed interesting mechanical properties. Their investigations which have been carried out to date in this field have been concerned with the synthesis¹⁻⁵, structure determinations⁶, and characterization^{7,8} of these copolyesters. The thermal and dielectric properties were also extensively investigated because the copolyesters showed very good properties in applications as high temperature insulation materials.

The goal of the present investigation was to determine the dynamic and static mechanical properties of a group of aromatic copolyesters having the following general structure:

in which $a + n = 1$ and the units A, T, and N were obtained, respectively, from the monomers 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A), terephthaloyl chloride, and 4,4'-binaphthol-1.

Polymerization conditions were chosen so as to obtain products containing different amounts of A and N units in the copolymers as well as different

sequence distributions of these units along the chains. The selection of copolyester samples for measurement was guided by an attempt to investigate their structure-property relationships. Table I contains characterization data for the copolyesters. The only mechanical properties of these polymers previously determined were the tensile strengths at room temperature⁹.

Sek and Smigasiewicz⁷ investigated the dielectric relaxation properties of terephthalic acid copolyesters containing an equal amount of A and N units but having different sequence distributions. At low temperatures at a frequency of 1 kHz they observed relaxation peaks in a temperature range of 215-220°K. The highest relaxation peak temperature was obtained for the copolyester with the highest content of N-T-A-T dyads.

Michailov and Eidelmant¹⁰ during dielectric relaxation investigations of poly[2,2-bis(4-hydroxyphenyl)propane terephthalate], the A-T homopolymer, found a low temperature β -relaxation and a high temperature α -relaxation. The latter showed a maximum at 481°K at a frequency extrapolated to 1 Hz.

Sek and Jedlinski⁸ determined the T_g values for copolyesters similar to those studied in the present investigation. They found limiting T_g values which showed a dependence on the content and distribution of the A and N units. Increasing the N content of the copolyesters increased the T_g, and the linear dependence of T_g on A and N contents allowed a determination of the extrapolated values of the T_g of the polyterephthalates of each of the bisphenol monomers, A and N. The values which they found were 484°K for the A-T and 560°K for the N-T homopolymers, respectively. For the copolyesters containing 30-70 mole % of N units ($n=0.3-0.9$), the T_g values were in a temperature range of 506-537°K. All

of these results suggest that for dynamic mechanical measurements two relaxation regions would be expected, a β -relaxation at about 200°K and an α -relaxation at about 500°K.

EXPERIMENTAL

Copolymer Samples

The terephthalic acid copolyesters of 4,4'-binaphthol-1, N monomer, and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A), A monomer, were prepared by low-temperature, solution polycondensation reactions⁵. The compositions of the copolyesters as previously described⁶ are listed in Table 1. Films were prepared by casting from about 10% (w/v) chloroform solutions onto glass plates floating on mercury. The solvent was evaporated at room temperature, and the films were dried under vacuum at increasing temperatures from 330 to 410°K until a constant weight was attained. Films of 100-20 microns thick were then used as cut strips or punched discs for the measurements. The samples were thermally treated in air at 470°K in most cases, but in some cases the treatment was performed at temperatures up to 520°K.

Measurements

Dynamic mechanical properties were determined on a Vibron Dynamic Viscoelastometer, Model DDV II from the Toyo Measuring Instruments Co. as follows: samples 40-50 mm in length, 3.2 ± 0.4 mm in width and 100 ± 20 μ m in thickness were used and the measurements were carried out within a temperature range of 100 to above 550°K under a dry nitrogen atmosphere at a heating rate of 1-2°K per minute and frequencies of 3.5, 11 and 110 Hz. Static mechanical properties were measured on a Tensilon (Toyo Instrument Co.) using samples identical to those used in the dynamic measurements. DSC measurements were carried out on a Perkin-Elmer DSC-2 instrument using 7-10 mg specimens, generally in the

form of discs, but in some cases powdered copolyesters were used as samples. Most of the measurements were carried out at a heating rate of 20°K per minute and the T_g was expressed as an average value.

DISCUSSION OF RESULTS

Mechanical Properties

The mechanical properties of the copolymers were found to depend on both the ratio of the bisphenol monomers and their sequence distribution along the copolyester chains. The storage modulus E' , the stress at yield σ_y , the elongation ϵ , and the Young's modulus E all showed this dependence within the entire range of temperatures investigated. In Tables 2 and 3 these properties are summarized while in Figures 1 and 2 the viscoelastic properties as a function of temperature at a frequency of 110 Hz are shown.

It was found that the higher the content of the binaphthol component, N, in the copolyesters, the better the strength properties achieved as measured by the stress at yield. Figure 3 shows the dependence of stress at yield and storage modulus on the copolyester composition. Furthermore, when considering two copolymers having similar N unit contents but different distributions: Sample 422 with a random distribution of N units and Sample 461 containing more alternating units, the latter had a higher stress at yield.

The $\tan \delta$ magnitudes in the α - and β -relaxation regions decreased with increasing N units in the series as shown in Figure 4. For the two copolyesters with similar contents of N units but different distributions, the lowest $\tan \delta$ value was shown by the copolyester with the higher N-T-A-T alternating dyad content. Outside of the relaxation regions, particularly in the range from room temperature to about 410°, the $\tan \delta$ differences for the various copolymers were insignificant and were essentially independent of temperature.

Annealing of the copolyester films below the T_g at 470°K resulted in E' , E and stress at yield increases and $\tan \delta$ and elongation decreases. In Table 4

and Figure 5 are shown the effects of annealing on these properties. The effects of annealing were greater on the static properties than on the dynamic properties. Such increases in σ_y and E together with decreases in E are commonly observed upon annealing many glassy polymers near their T_g . For example, similar results to those reported here were obtained on measurements on PVC films¹¹. It is thus not unreasonable that such effects should be observed here at temperatures about 200°K below T_g .

Relaxation Processes

In the range of the test temperatures from 100-570°K two main transition regions were observed for all samples. It was possible to observe a distinct relaxation, the temperature of which occurred at 211-212° and at 221°K at 110 Hz for the copolymers containing either lower (Samples 483 and 422) or higher (Sample 459, 460, and 461) A-T-N-T alternating dyad concentrations. This mechanical relaxation occurred in a temperature range in which a dielectric β -relaxation was also found. Comparing the results for the copolyester examined by Sek and Smigasiewicz⁷ with those for Sample 422, both of which had similar compositions, it may be noted that the temperatures of the $\tan \delta$ maxima corresponded well to each other, taking into account the frequency differences of the measurements: 214.6°K for their copolyester at 1 kHz and 211°K for Sample 422 copolyester at 110 Hz.

The peaks for both the mechanical loss factor $\tan \delta$ and loss modulus E'' were less distinct than those of the dielectric loss factor, particularly at lower frequencies. The $\tan \delta$ magnitudes of the copolyesters containing a more alternating dyad sequence, Samples 459 and 461, decreased with increasing temperature to a lesser extent than those of the other copolyesters, and a weak

maximum was observed at ambient temperature. However, after annealing these relaxations became more distinct. At ambient temperature they were almost linear and the $\tan \delta$ values were lower.

The activation energy, ΔH_a , determined from the Arrhenius plot of the β -transition of the annealed form of Sample 483 was 51 ± 5 kJ/mole. This value is close to that obtained from dielectric β -relaxation of a closely related copolyester (44.4-50.2 kJ/mole) as previously reported⁷. However, the value of ΔH_a was higher for the copolyester with the highest A-T-N-T dyad concentration. The calculated value of 75 ± 10 kJ/mole and the relaxation peak temperature showed that a more uniform distribution of N elements lead to a β relaxation which required a higher energy input for its activation. The agreement between the dielectric and mechanical β -relaxations with regard to temperatures and activation energies indicate that they arise from a similar mechanism, perhaps from rotation of chain fragments including the ester group. The $\tan \delta$ magnitudes increased with increasing A content, but their temperatures remained almost unchanged.

The value of ΔH_a for the dielectric β -relaxation given by Mikhailov and Eidelmant¹⁰ for poly[2,2-bis(4-hydroxyphenyl)propane terephthalate], the A-T homopolymer, of 50 kJ/mole is practically equal to that of the copolyesters studied here. Hence, it is believed that for the present copolymers, in the β -relaxation process the motions of the $-T-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-O-A-$ fragments were dominant. This suggestion is reinforced to some extent by the trends of the $\tan \delta$ magnitudes within the relaxation region, see Figure 4 and Table 2.

At a $\tan \delta$ value of 0.04, the viscoelastic properties changed significantly at 110 Hz. The basic transition, the increase of $\tan \delta$ from 0.04 to maximum values, proceeded over a relatively narrow temperature range of only 60-74°K.

The storage modulus decreased from 1000 to 100 MPa over a range of 35°K for the random copolyesters and over a range of 29°K for the most alternating copolyester, Sample 421. For the copolyester which contained the greatest amount of N elements, Sample 459, the E' decreased at the α transition only by 1.6 decades. The other copolyesters showed a greater decrease. This rather small modulus change accompanying the glass transition exhibited by Sample 459 is similar to those observed for filled polymers or multiphase polymers¹².

In Table 5 are collected values of the peak temperature in E'' , the characteristic temperatures of $\tan \delta$, and the activation energies in the α -relaxation region, as well as the DSC T_g values. The E'' peak temperatures for random copolyesters shifted toward lower temperatures when the content of N units increased. It occurred at the highest temperature for the copolyester having an excess of alternating dyads. The $\tan \delta$ temperatures for the copolyesters under examination were virtually identical and all of them were in the range of 541-545°K.

In the annealed copolyesters the values of $\tan \delta$ below the α -transition region decreased, E' increased by about 10%, and the onset of the significant increase in the damping properties was shifted up by about 20°K in comparison with unannealed copolyesters. The damping properties, $\tan \delta$ and E'' of both Samples 483 and 459 after annealing were almost identical, although their N contents were quite different. It appears that the moving chain segments in the α -relaxation region did not include the N units. This conclusion is tentative, however, because of the low molecular weights of the copolyesters and the differences in molecular weight among the various samples.

DSC Measurements

The DSC thermograms for the first heating cycles showed broad maxima at temperatures of 40-60°K below the beginning of the glass transition regions. The range of temperatures at which these maxima occurred corresponded with some $\tan \delta$ variations as shown in Figures 1, 2, and 5, as observed in dynamic mechanical measurements. These maxima may be observed both in powdered precipitated polymers and in films, thus this phenomenon could not be attributed to film formation. Annealing of the films at 470°K caused a gradual shift of the maxima towards higher temperatures as well as an increased sharpness. Finally, the maxima occurred at the upper range of the observed glass transition interval as shown in Figures 6 and 7.

This behavior is typical of a broad range of glassy polymers and has been well explained on the basis of enthalpy relaxation. During a second heating cycle carried out after an initial heat treatment which exceeded T_g by about 50°K, the maxima were no longer observed and the typical glass transitions were seen as a step in C_p values, see Figure 6, as would be expected on the basis of the enthalpy relaxation mechanism. It is interesting to note that the glass transition region was similar in all the tested polymers and did not depend significantly on the composition of the copolyesters. However, as previously mentioned, the effects of molecular weight on the observed T_g have not been considered in detail. For similar copolyesters of different molecular weights a slightly higher T_g was observed for the higher molecular weight copolyester, but the initial point of transition of all the copolyesters was at 482-483°K at a heating rate of 20°K min⁻¹. DSC measurements were made on the homopolymers, Samples 457 and 456. During the first heating cycle in the thermogram of the A-T

homopolymer no glass transition was observed but an endothermic peak characteristic of a melting transition occurred at 513-552°K. During a second heating cycle carried out just after quenching the sample which had been previously heated up to 575°K, only the glass transition was recorded corresponding to that of the other copolyesters, see Figure 8.

In the thermograms of the N-T homopolymer, Figure 8, an enthalpy relaxation peak was observed at 700°K in the first heating cycle, and a T_g at about 650°K was seen in the second heating cycle. The second heating cycle was carried out after the sample was heated up to 725°K and quenched. The DSC Data are collected in Table 5.

SUMMARY

The samples studied belonged to a series of copolyesters containing two bisphenols which differed in their molecular rigidity. The presence of large, stiff units of the N monomer controlled the properties of these copolyesters. The dynamic and static moduli of elasticity and the stress at yield increased with increasing quantities of these N units. This effect became greater the more uniform the distribution of these units. The glass transition observed by DSC did not depend either on the copolyester composition or on the sequence distribution and corresponded to that of the A-T homopolymer. It is possible that the N-T units impart a form of a self-reinforcing effect in the copolymer samples by a microphase separation. In any case, the combination of high mechanical properties and high T_g values should make these copolymers of use as engineering thermoplastics at temperatures up to 450°K. There is as yet no explanation for the small storage modulus loss observed at about 440° in the annealed copolyesters. This property is characteristic of many aromatic polymers¹³, but its occurrence has not been hitherto explained.

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TABLE 1. Structural characteristics of the terephthalic acid, T, copolyesters of 4,4'-binaphthol-1, N, and 2,2-bis(4-hydroxyphenyl)propane, A^a.

Sample Number	$\bar{M}_n$	N content ^b moles	Dyad Contents, mole %			Block Length		Degree of Randomness B
			A-T-A-T	A-T-N-T	N-T-N-T	LAT	LNT	
457	--	0	100	0	0	-	-	0
483	4100	0.27	55	36	9	4.0	1.5	0.91
460	8700	0.39	38	46	16	2.7	1.7	0.98
422	7600	0.43	35	43	22	2.6	2.0	0.88
461	4900	0.47	20	66	14	1.6	1.4	1.3
459	--	0.55	21	49	30	1.9	2.2	0.99
456	--	1	0	0	100	-	-	0

^aData taken from Reference 5.

^bN + A = 1

TABLE 1. Structural characteristics of the terephthalic acid, T, copolyesters of 4,4'-binaphthol-1, N, and 2,2-bis(4-hydroxyphenyl)propane, A^a.

Sample Number	$\bar{M}_n$	N content ^b moles	Dyad Contents, mole %			Block Length		Degree of Randomness B
			A-T-A-T	A-T-N-T	N-T-N-T	LAT	LNT	
457	--	0	100	0	0	-	-	0
483	4100	0.27	55	36	9	4.0	1.5	0.91
460	8700	0.39	38	46	16	2.7	1.7	0.98
422	7600	0.43	35	43	22	2.6	2.0	0.88
461	4900	0.47	20	66	14	1.6	1.4	1.3
459	--	0.55	21	49	30	1.9	2.2	0.99
456	--	1	0	0	100	-	-	0

^aData taken from Reference 5.

^bN + A = 1

TABLE 2. Dynamic mechanical properties of the terephthalic acid, T, copolyesters of the 4,4'-binaphthol-1,N, and 2,2-bis(4-hydroxyphenyl)propane, A, determined at 110 Hz.

Sample Number	N Content ^a moles	Storage modulus, E', in MPa at temperature indicated, °K				Mechanical loss factor, tan δ, at temperature indicated, °K			
		140	295	475	560	213 ^b	295	400	543 ^b
483	0.27	4930	2490	1430	16	.0405	.0165	.0170	0.85
460	0.39	5700	3190	1750	29	.0290	.0210	.0178	0.76
422	0.43	5050	3110	1700	27	.0385	.0175	.0180	0.78
461	0.47	5650	3840	2170	37	.0300	.0205	.0160	0.74
459	0.55	7990	4540	2200	52	.0250	.0185	.0170	0.66

^aN + A = 1

^bRelaxation peak temperatures

TABLE 3. Mechanical properties of the terephthalic acid, T, copolyesters of the 4,4'-binaphthol-1, N, and the 2,2-bis(4-hydroxyphenyl)propane, A, determined in tensile tests.

Sample Number	N content moles	Stress at yield, σ_y MPa	Elongation at yield, ϵ_y %	Young's modulus, E MPa
483	0.27	53.5	7.0	1700
460	0.39	58.5	4.8	1860
422	0.43	57.9	4.9	1800
461	0.47	61.0	7.0	1840
459	0.55	66.5	5.4	2130

TABLE 4. Mechanical properties of Sample 460^a before and after annealing at 470°K for 45 hours.

Treatment	Static mechanical properties at 295°K in tensile test					
	Stress, MPa		Elongation, %		Young's modulus E MPa	
	at yield σ_y	at break σ_B	at yield ϵ_y	at break ϵ_B		
Unannealed	58.8	72.5	4.8	45.4	1860	
Annealed	--	99.1	--	7.3	2600	
	Dynamic mechanical properties at 110 Hz					
	Storage modulus E', MPa at temperature indicated, °K				Mechanical loss factor tan δ at temperature indicated, °K	
	295	475	520	560	295 475 520 545 ^b	
	unannealed	3190	1750	580	29	0.0210 0.0415 0.385 0.76
	annealed	3550	2250	600	28	0.0120 0.0238 0.375 0.77

^aContains 39 mole % N units; see Table 1

^bPeak temperature

TABLE 5. Mechanical and thermal properties of the terephthalic acid, T, copoly-
ester of the 4,4'-binaphthol-1, N, and the 2,2-bis(4-hydroxyphenyl)-
propane, A, determined in the glass transition region.

Sample Number	N Content moles	Characteristic transition temperatures °K			Transition Energy, ΔH_g J/g
		Tg ^b	E'' peak at 110 Hz	Tan δ peak at 110 Hz	
483	0.27	492	520	542	.92
460	0.39	495	519	545	1.17
422	0.43	492	515	544	1.13
461	0.47	496	520	543	1.21
459	0.55	493	509	541	1.08
457 ^b	0	495	--a	--a	1.05

^aMechanical preoperties not determined due to insolubility of polymers.

^bApproximate DSC value obtained at a heating rate of 20°K/min.

FIGURE CAPTIONS

- Figure 1: Dynamic mechanical behavior at 110 Hz for Sample 483 containing the minimum (27 mole %) and Sample 459 containing the maximum (55 mole %) of N units.
- Figure 2: Dynamic mechanical behavior at 110 Hz for copolyesters with similar contents of N units but different sequence distributions: Sample 422 - random distribution, 43 mole % N; Sample 461 - tendency toward alternating distribution, 47 mole % N.
- Figure 3: Stress at yield and Young's modulus changes as a function of copolyester composition.
- Figure 4: Tan δ magnitudes in relaxation regions as a function of copolyester composition.
- Figure 5: Comparison of dynamic mechanical behavior for unannealed and annealed copolyesters; the symbol A after the sample number is for copolyesters annealed at 470° for 45 hours.
- Figure 6: DSC thermograms for Sample 422 (43 mole % N units):
- 1 - first heating cycle
 - 2 - second heating cycle after being heated to 550°K during the first heating run
 - 3 - first heating cycle after annealing the copolyester at 470°K for 45 hours.
- Figure 7: DSC thermograms of the first heating cycle for Sample 483 (27 mole % N units) annealed at 470°K for different times as indicated.

Figure 8: DSC thermograms for the two homopolyesters in the series: Samples 457, the A-T homopolymer, and 456, the N-T homopolymer:

- 1 - first heating cycle
- 2 - second heating cycle.