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Thermotropic copolyesters modified with nonmesogenic rigid groups

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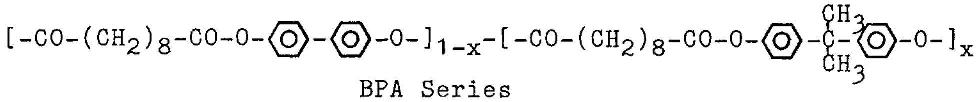
SUMMARY

Two series of copolyesters of sebacic acid, 4,4'-biphenol and a nonmesogenic rigid diol which was either bisphenol A (BPA series) or hydroquinone (HQ series) were prepared by melt polycondensation. The thermal transitions and melt birefringence which were investigated by DSC and polarized microscope respectively. Homopolyester of 4,4-biphenol and sebacic acid (PB8) was found to show two transition temperatures corresponded to T_m and T_i respectively. For the BPA series, the incorporation of amorphous bisphenol A unit by copolymerization decreased both T_m and T_i and completely destroyed the mesophase as the content of bisphenol A unit was over 50 mole%. For the HQ series, the incorporation of crystalline hydroquinone unit decreased T_m to more extent, but decreased T_i to less extent as compared to the BPA series. When the hydroquinone unit was as high as 80 mole%, the mesophase was completely destroyed.

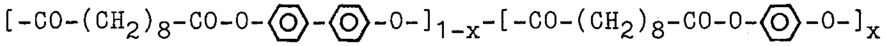
INTRODUCTION

The homopolyesters of 4,4'-biphenol and various aliphatic diacids were found to exhibit liquid crystalline behavior[1-5]. These main chain thermotropic polyesters were characterized as a mesogenic group linkaged with a flexible spacer. The influence of structure of spacers and the effect of copolymerization of various spacers on their liquid crystalline behavior were investigated in details. It will be very interesting to understand the effect of a nonmesogenic group on their properties. Krigbaum and coworkers [5] prepared the copolyesters of 4,4'-biphenol, 2,6-dihydroxynaphthalene and aliphatic dicarboxylic acids. When pimelic acid was used, the copolyesters showed only nematic phase, and the liquid crystalline behavior was destroyed completely as the content of nonmesogenic rigid group was over 60 mole%. When sebacic acid was used, the presence of nonmesogenic group fist destroyed some smectic order, and nematic phase formed. Once the content of nonmesogenic groups was over 70 mole%, smectic phase disappeared and only nematic phase was observed. It will be interesting if the nonmesogenic groups are even different.

In this study, two series of copolyesters, namely, BPA, and HQ series, were prepared. The effect of the nonmesogenic bisphenol A and hydroquinone units on the transition temperature and liquid crystalline properties was investigated. The chemical structure of the copolyesters is shown below:



BPA Series



HQ Series

EXPERIMENTAL

Sebacic acid and bisphenol A were Merck reagent grade, and 4,4'-biphenol, and hydroquinone were obtained from Tokyo Chemical Industry Co., Ltd. 4,4'-Biphenol diacetate (T_m: 165-166°C), and hydroquinone diacetate (T_m: 125 - 126°C) were obtained by reacting 4,4'-biphenol and hydroquinone respectively with acetic anhydride followed by recrystallizing twice from acetone solution. Bisphenol A diacetate (T_m:93 - 94°C) was obtained by a similar method but recrystallization was carried out in ethanol. The homopolyesters and copolyesters were prepared by reacting sebacic acid with equal moles of the bisphenol diacetates. Typical procedure was as follows. Under nitrogen gas, 0.025 mole of sebacic acid, 0.0125 mole of 4,4'-biphenol diacetate, and 0.0125 mole of bisphenol A diacetate were reacted at 240°C in a 1L reactor. After most acetic acid was distilled out, vacuum was applied slowly to about 0.5 torr for two hours. The obtained copolyester was denoted as BPA50 which indicates that the content of bisphenol A unit was 50 mole%.

The intrinsic viscosity of the copolyesters in phenol/TCE (syn-tetrachloroethane) at 30°C was determined by a Ubbelohde Viscometer. The thermal properties were determined by a Perkin Elmer DSC-2 under nitrogen. The liquid crystalline texture was observed on a Leitz Polarizing Microscope.

RESULTS AND DISCUSSION

The molar fraction of bisphenol A unit or hydroquinone unit and the corresponding intrinsic viscosity of the two series of copolyesters are shown in Table I.

Typical second run DSC thermograms of some copolyesters are shown in Figure 1. The peak temperature was taken as transition temperature. By combination with the observation on the polarized microscope, the transition from crystalline phase to mesophase (melt birefringent one) or isotropic phase was taken as T_m and that corresponded to the transition from mesophase to isotropic phase was taken as T_i.

The transition temperatures of the two series of copolyesters are listed in Table II. The homopolyester of 4,4-biphenol and sebacic acid (PB8) was found to show two transitions corresponded to T_m and T_i respectively. The mesophase was identified as smectic phase through the observation of the development of fan-like texture on the polarized microscope. As shown in Table II, the presence of nonmesogenic rigid unit had different influence on the thermal transitions for the two

Table I. The molar fraction of nonmesogenic unit and intrinsic viscosity of the copolyesters.

	Molar fraction x	Intrinsic viscosity(dL/g)
PB8	0	0.61
BPA10	0.1	0.70
BPA20	0.2	0.73
BPA30	0.3	0.94
BPA40	0.4	0.52
BPA50	0.5	0.20
BPA60	0.6	0.29
BPA70	0.7	0.24
BPA80	0.8	0.31
BPA90	0.9	0.23
BPA100	1	0.55
HQ10	0.1	0.65
HQ20	0.2	0.72
HQ30	0.3	0.80
HQ40	0.4	0.61
HQ50	0.5	0.64
HQ60	0.6	0.64
HQ70	0.7	0.56
HQ80	0.8	0.43
HQ90	0.9	0.24
HQ100	1	0.69

Table II. The thermal transition temperatures (°C) of the copolyesters.

	T_m	T_{M-M}	T_i
PB8	212		283
BPA10	205		266
BPA20	195	240	260
BPA30	170		198
BPA40	165		188
BPA50	160		
BPA60	151		
BPA70	130		
BPA80		No endotherm	
BPA90		No endotherm	
BPA100		No endotherm	
HQ10	177		269
HQ20	151		259
HQ30	133		235
HQ40	121		234
HQ50	125		221
HQ60	127		202
HQ70	147		162
HQ80	160		
HQ90	164		
HQ100	168		

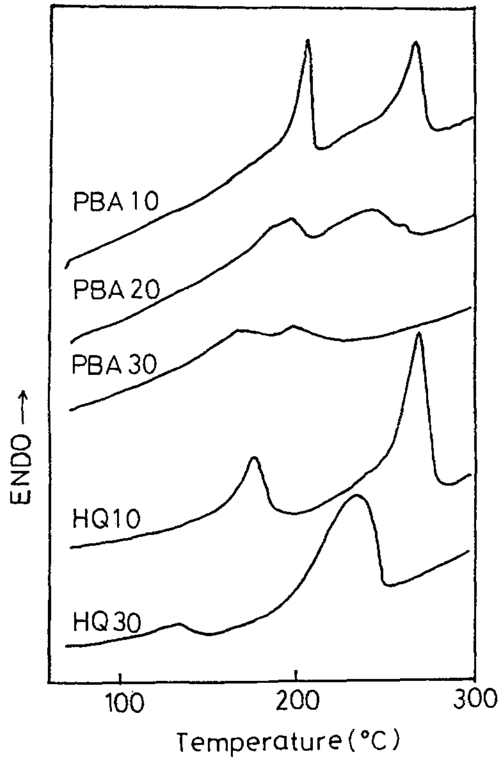


Figure 1. Typical DSC thermograms of some copolyesters.

series of copolyesters.

The homopolyester of sebacic acid and bisphenol A was amorphous as indicated by no endotherm of the DSC thermogram. For the BPA series, the incorporation of amorphous bisphenol A unit by copolymerization decreased both T_m and T_i. When the content of bisphenol A unit was below 20 mole%, the mesophase also exhibited smectic fan-like texture. BPA20 exhibited three transition temperatures (T_m, T_{M-M} and T_i). No well-defined texture was observed between T_{M-M} and T_i due to its high melt viscosity. However, as described by Krigbaum and coworkers, the presence of nonmesogenic rigid unit could cause formation of nematic phase, nematic phase might also be formed between T_{M-M} and T_i for BPA20. As the content of bisphenol A unit was between 30 and 40 mole%, only two transition temperatures were again observed. BPA50 showed only one endotherm and no melt birefringence, thus the mesophase was completely destroyed the mesophase as the bisphenol A unit was over 50 mole%.

The homopolyester of sebacic acid and hydroquinone exhibited one transition and was a crystalline polymer. The influence of nonmesogenic rigid unit on the thermal transition of HQ series was considerably different to BPA series as shown in Table II. For the HQ series, the incorporation of crystalline hydroquinone unit decreased T_m to more extent, but decreased T_i to less extent as compared to the BPA series. No development of a third transition temperature was observed for HQ series. The relationship between T_m and composition for HQ series showed eutectic behavior as shown in Table II. When the content of hydroquinone unit was as high as 80 mole%, the mesophase was completely destroyed.

In conclusion, the influence of two different nonmesogenic rigid units on the thermal transitions of two series of copolyesters was found to be different. The effect of these two nonmesogenic rigid units was also considerably different to nonmesogenic 2,6-dihydroxynaphthalene unit described in the literature [6].

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