

## Synthesis and Characterization of Random Copolyesters of Aromatic Diols

SAYEEDA SULTANA\*, SIVARAMA KRISHNAN†, S. GUNASEKARAN‡ and  
T. VENKATARAMAN#

Department of Chemistry, St .Peter's Engineering College  
Ayadi, Chennai-600 054, India  
E-mail: sayeeda2006@yahoo.com

Copolyesters based on adipoyl chloride with aromatic diols were synthesized by solution polycondensation method. The copolyesters were characterised by IR, <sup>1</sup>H NMR, UV-Visible spectral studies. Solubility was checked in some common organic solvents and they showed better solubility in acetone and dimethyl formamide. The solubility of copolyesters depends on the rigidity of polymer backbone, molecular weight and interaction between polymer and solvent molecules. The random units distributed in the copolyester chain were assigned based on spectral studies.

**Key Words:** Copolyester, Synthesis, Structure.

### INTRODUCTION

Aromatic polyesters are designed in a broad sense as polyesters that contain aromatic components in the main chain. Polyarylates, the class of high performance engineering plastics<sup>1</sup> are polyesters synthesized with one or more aromatic moieties in the main chain. Many copolyesters have been synthesised by solution condensation of diols with dicarboxylic acids in an inert solvent, dichlorobenzene<sup>2-4</sup>. The need of copolyester with high melting point and chemical resistance led to the preparation of many industrially important copolyesters by Eastman Kodak Co.<sup>5</sup>. Synthesis of random copolyesters of ethylene glycol, butanediol<sup>6</sup>, propanediol<sup>7</sup> and dibromo-*p*-acetoxy benzoic acid<sup>8</sup> were reported by Balakrishnan *et al.* Copolyesters composed of aliphatic and aromatic units such as 1,2-dichloro benzene, propane-1,3-diol, butane-1,4-diol, adipic acid and terephthalic acid combined in an appropriate ratio has proved to be biodegradable<sup>9-11</sup>. The biodegradation behaviour of copolyesters which contain aliphatic and aromatic sub units are dependent on composition, chain length and

\*Department of Chemistry, D.G. Vaishnav College, Chennai-600 100, India.

†Reader in Physics, Pachaiyappa's College, Chennai-600 030, India.

#Principal, Adhiparasakthi College of Arts and Science, Kalavai-632 506, India.

sequence distribution of aliphatic and aromatic units, crystallinity and melting temperature<sup>12,13</sup>. In the present work, copolyesters of aromatic diols were synthesized by polycondensation method following the procedure given by Polk *et al.*<sup>14</sup> and the structure was elucidated by spectral studies.

## EXPERIMENTAL

1,2-Dichloro benzene and petroleum ether were dried over anhydrous calcium chloride and used. Rechem samples of resorcinol and quinol were recrystallized.

**Synthesis of poly[oxy(1,3-phenylene)-oxyadipoyl-co-oxy-(2,3-naphthyl)-oxyadipoyl] (PRNA):** A 500 mL three necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reflux condenser with guard tube was charged with 0.03 mol (3.3034 g) of resorcinol 0.015 mol (2.4026 g) of 2,3-dihydroxy naphthalene, 0.045 mol (6.5 mL) of adipoyl chloride and 250 mL of *o*-dichlorobenzene. The mixture was heated to reflux for 25-30 h at 140-160°C in nitrogen atmosphere with constant stirring. After cooling the contents the mixture was poured in to about 500 mL of petroleum ether and allowed to stand for 24 h and filtered. The co-polyester was washed with deionized water, dissolved in minimum amount of acetone and the clear solution was poured into water to get pure shiny black co-polyester (yield 60-65%).

**Synthesis of poly [oxy(1,4-phenylene)-oxyadipoyl-co-oxy-(2,3-naphthyl)-oxyadipoyl] (PQNA):** In the same experimental set up as above a mixture of 0.03 mol (3.3034 g) of quinol, 0.015 mol (2.4026 g) of 2,3-dihydroxy naphthalene, 0.045 mL (6.5 mL) of adipoyl chloride and 250 mL of 1,2-dichloro benzene was taken and refluxed for 25-30 h at 140-160°C. A similar procedure was adopted to get dry copolyester, (yield *ca.* 80 %).

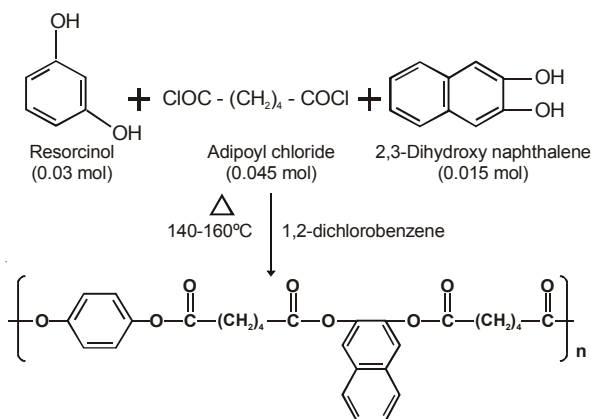
## RESULTS AND DISCUSSION

The copolyesters PRNA and PQNA are stable at room temperature. They are soluble in acetone and dimethyl formamide and insoluble in benzene and carbon tetrachloride.

The UV-Visible spectra were recorded in acetone as solvent. The UV-Visible spectra of the copolyesters PRNA and PQNA are similar since both contain the same chromophore as substituted naphthalene ring moiety. The absorption maxima occur at 300-320 nm which may be due to  $\pi \rightarrow \pi^*$  transitions in naphthalene. The structure of co-polyesters PRNA and PNQA was elucidated by IR spectrum. The IR spectra were taken by incorporating into KBr pellets in the frequency range of 4000-400  $\text{cm}^{-1}$ . The IR spectrum of the copolyester PRNA shows characteristic absorption at 1693  $\text{cm}^{-1}$  due to  $>\text{C}=\text{O}$  group. The presence of (C–O) stretching vibration of ester group

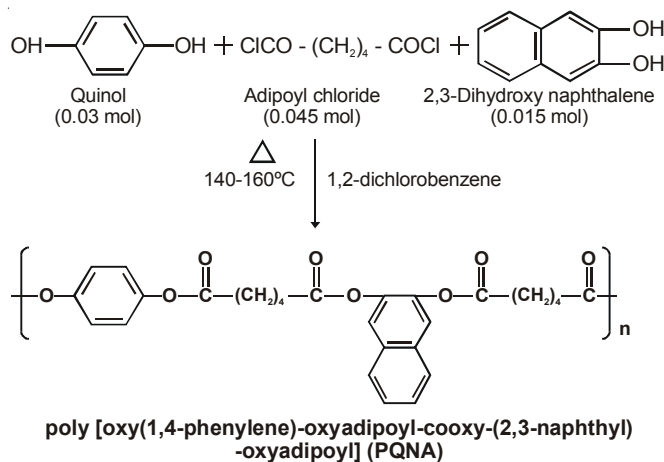
is confirmed by the presence of strong bands at 1278 and 1193  $\text{cm}^{-1}$ . This indicates that the condensation between diacid chlorides and diols has occurred resulting in ester formation. The presence of bands at 1462 and 3401  $\text{cm}^{-1}$  indicates the presence of aromatic groups in the polymer chain. The aliphatic C–H stretching vibration at 2879  $\text{cm}^{-1}$  and aliphatic C–H bending vibration at 927  $\text{cm}^{-1}$  show the presence of aliphatic group in the polymer chain. The IR spectrum of the co polyester PQNA shows characteristic absorption at 1750  $\text{cm}^{-1}$  due to  $>\text{C}=\text{O}$  group. The presence of (C–O) stretching vibration of ester group is confirmed by the presence of strong band at 1249 and 1188  $\text{cm}^{-1}$ . This indicates that the condensation between diacid chlorides and diols has occurred resulting in ester formation. The presence of peaks at 1507 and 3452  $\text{cm}^{-1}$  indicates the presence of aromatic groups in the polymer chain. The aliphatic C–H stretching vibration at 2874  $\text{cm}^{-1}$  and aliphatic C–H bending vibration at 929  $\text{cm}^{-1}$  show the presence of aliphatic group in the polymer chain.

The  $^1\text{H}$  NMR spectra of the copolyesters PRNA and PQNA were taken in  $\text{d}_6$  acetone as solvent and TMS as internal standard. The  $^1\text{H}$  NMR spectrum of PRNA shows signal at  $\delta = 2.10$ -2.13 ppm due to the protons of the ester group. Hence the presence of ester linkage is confirmed. The signal at  $\delta = 7.02$ -7.95 ppm is due to the aromatic protons of resorcinol and naphthalene. The signal around 2.8 ppm corresponds to methylene protons of acid chloride. The  $^1\text{H}$  NMR spectrum of PQNA shows signal at  $\delta = 2.12$ -2.313 ppm due to the protons of the ester group. The signal at  $\delta = 7.2179$ -9.22 ppm shows aromatic protons of quinol and naphthalene. The signal due to methylene protons are shifted downfield and are seen around  $\delta = 3$  ppm. Based on the spectral data it may be concluded that the following units are randomly distributed in the copolyesters PRNA and PQNA as shown in **Schemes I and II**.



**Poly[oxy(1,3-phenylene)-oxyadipoyl-cooxy-(2,3-naphthyl)-oxyadipoyl] (PRNA)**

**Scheme-I**



Scheme-II

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