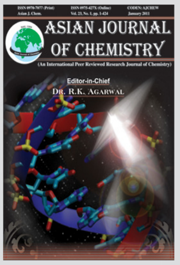
Asian Journal of Chemistry; *Vol. 23, No. 8 (2011), 3428-3430*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Thermogravimetric Analysis of 2,3-Butadiene Based Random Block Copolyesters

G. ELANGO[1,*] and S. GUHANATHAN[2]

[1]Department of Chemistry, Government Arts College, Tiruvannamalai-606 603, India
[2]Research and Post Graduate Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore-632 002, India

*Corresponding author: Tel: +91 4175 237130; E-mail: sai_gugan@yahoo.com

(*Received*: 4 September 2010; *Accepted*: 18 April 2011) AJC-9818

Three copolyesters were synthesized using 2,3-butane diol with phthaloyl chloride. 2,5-Ditertiary butyl quinol, 1,2-propane diol and 1,5-naphthalene diol were used as another diols for the synthesis of random copolymer. Thermal studies were carried out using DSC and TGA. Results of the investigation confirm relatively new entry copolymers in the family of thermally stable copolymers.

Key Words: Copolymers, Diol-diacid, Thermal studies.

INTRODUCTION

A polymer is a large molecule built up by repetition of smaller chemical units. This repetition may be linear or branched or interconnected to form three dimensional networks. These repeated units are derived from monomers, which combine together and form a macro molecule. The process of formation of a macro molecule is termed as polymerization. The number of repeat units in the chain specifies the length of the polymer chain. This is called degree of polymerization. Natural polyesters have been known since ancient times and have been widely used by mankind. Such substances include amber, dammer, shellac, copal, *etc*.

Polyesters attract significant interest, despite inferior mechanical properties. Transition temperature and properties of the copolyesters can be varied by altering the comonomer composition. Polyesters are the most important and widely used class of polymers which fall under heterochain macro molecular compounds possessing carboxylate esters as a part of the repeating unit. They are distinguished from other esters in which carboxylate ester group forms a part of substituent moiety attached to the backbone structure. Polyesters are usually prepared by the condensation of a diacid or its derivatives with diols. The vast interest in commercial utilization of copolyesters has necessitated the determination of composition and microstructure as an important adjunct to polymer technology. Aromatic polyesters are designated in a broad sense as polyesters that contains one or more aromatic components in the main chains and therefore include aliphatic polyacrylates and aromatic ones, as well as aliphatic-aromatic polyesters such as commercially, important poly-(ethylene terephthalate) and poly-(butylene terephthalate)[1].

The high melting temperature or softening temperature of most polyarylates make their processing into articles difficult, because such high softening temperature are often close to the decomposition temperature of polymers. Films of soluble high melting polyarylates were therefore prepared by casting from their solutions[2]. Walton and Philip[3] synthesized 1,4-phenylene-terephthalate polyesters bearing a methyl, methoxy or halogen substituents on one or both aromatic rings of the repeat units. These polymers were reported to have melting temperature in excess of 350 ºC. Extensive studies[4-9] have been done on fully aromatic thermotropic polyesters based on the hydroquinone or terephthalic acid monomers with asymmetric substitutents. A few investigations have been carried out on fully aromatic thermotropic polyesters based on 3,4'-benzophenone dicarboxylic acid.

The present work deals with the synthesis and characterization of three random copolyesters containing aliphatic as well as aromatic moieties in the main chain. The introduction of aliphatic groups in the polymer backbone may increase the solubility and decrease the melting temperatures. The polyesters are synthesized by the polycondenstaion of diacid chlorides and diols in *o*-dichloro benzene solution.

EXPERIMENTAL

Table-1 summarizes the following diacid chlorides used are proposed to be in the present work were synthesized and reported elsewhere[10].

TABLE-1
LIST OF MATERIALS

Monomers	Make
Phthaloyl chloride	Lancaster
1,2-Propane diol	Sigma
2,3-Butane diol	Sigma
Quinol	Merck
2,5-Ditertiary butylquinol	BDH
1,5-Naphthalene diol	Lancaster

The thermal characterization was alone selected for personal attention towards thermally stable family of polymers. Hence, TGA for three polymers were recorded with Perkin-Elmer thermogravimetric analyser (TGA-7). DSC thermograms were recoded with Perkin-Elmer differential scanning calorimeter (DSC-204) with a heating rate of 10 ºC/min was maintained over a temperature range of 50-550 ºC.

RESULTS AND DISCUSSION

Thermogravimetric technique measures the mass of a substance as a function of temperature while the substance is subjected to a controlled temperature program. Any reaction that results in weight change of the sample is recorded as weight *versus* temperature (dynamic) or weight *versus* time (isothermal). Equations were derived for non-reversing conditions so that rate dependant parameters such as energy of activation and order of reaction may be calculated from a single experimental curve. For this purpose, a relationship between specific rate and temperature was assumed[11,12].

$$K = A.e^{-E/RT}$$

where K is the rate constant, A is the frequency factor and E is the activation energy. One of the early attempts to estimate activation energy, frequency factor and reaction order for the pyrolysis of organic compounds. The methods proposed were tedious and involved many assumptions.

Several researchers developed a widely used method for the determination of reaction kinetics using the thermobalance[11,12]. In any polymerisation pyrolysis, the TG trace follows relatively simple sigmoidal path. Thus, the sample weight decreases slowly as degradation begins, then decreases rapidly over a comparatively narrow temperature range and finally comes off as the reactant becomes spent. The shape of the trace depends primarily on the kinetic parameters involved, *i.e.*, on reaction order (n), frequency factor (A) and the activation energy (E). The values of these parameters can be of major importance in polymer degradation and in the estimation of thermal stability.

The thermal stability of the copolyesters can be determined by TG. It can also be used to determine the kinetic parameters of degradation of copolyesters. The continuous weight loss curves for the thermal degradation of three copolyesters are given in Figs. 1-3. The degradation of all copolyesters was carried out in nitrogen atmosphere at a heating rate of 20 ºC/min.

These thermograms suggest that the copolyesters are thermally stable upto 225 ºC. There are two steps in the degradation. The first degradation step starts around 225 ºC and about 80 % of the copolyesters were degraded in this step. The second stage of degradation starts around 275 ºC and in this state *ca.* 97 % of the copolyesters get degraded[12].

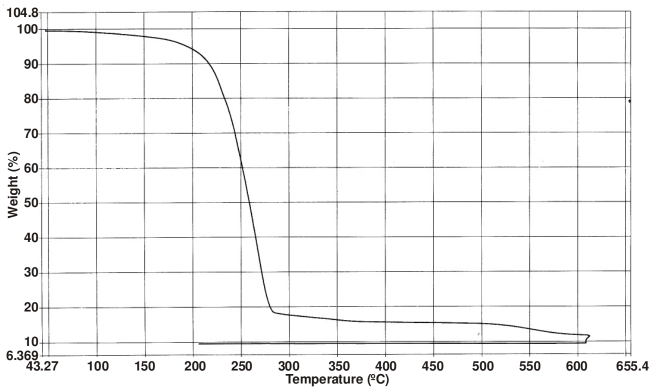


Fig. 1. TG thermograms of Random Copolyester-P3BPD

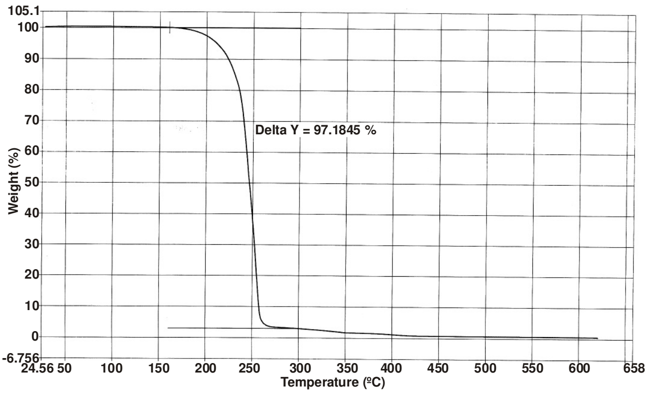


Fig. 2. TG thermograms of Random Copolyester-P3BPP

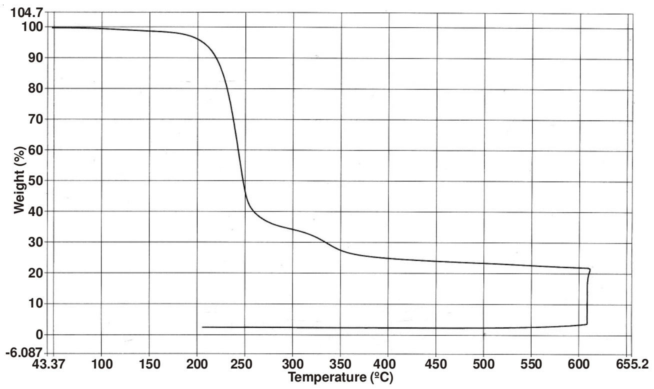


Fig. 3. TGA thermograms of Random Copolyesters P3BPN

Table-2 shows that 70 % of the polyesters were degraded at about 250-340 ºC except PQP5N. For 70 % degradation, 620 ºC was needed for this polyester. This may be due to the presence of rigid rod and crank shaft mesogens. After 340 ºC only about 10 % of the copolyesters were degraded. At 400 ºC, 90 % degradation was observed.

TABLE-2
THERMAL STABILITY OF COPOLYMERS

Copolyesters	Temperature (ºC) corresponding weight loss								
	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %	90 %
P3BPD	222	238	248	250	263	270	275	285	–
P3BPP	225	240	242	245	247	250	253	256	–
P3BPN	220	233	238	244	247	263	338	–	–

It is evident from the degradation temperature of copolyesters that the copolyester P3BPP degraded at lower temperature compare to others. This may be due to the presence of aliphatic mesogens. All other nine copolyesters show high degradation temperature due to scission of the bonds in the copolyesters containing phenylene ring. Similar observations were reported in previous investigations[13-17].

Conclusion

Three random copolymers were synthesized and characterized for thermally stable polymers. Inclusion of aliphatic in aromatic increases their solubility and decreases the melting temperature and also enhances the thermal stability. These copolymers with mentioned improved thermal properties have potential use in the liquid crystalline for specific applications.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged Prof. T. Venkataraman, Director, Sri Venkateswara College of Engineering and Technology, Thiruvallur for guidance and valuable suggestions.

REFERENCES

1. R.W. Lenz, *J. Polym. Sci. Polym. Symp.*, **72**, 1 (1985).
2. M.B. Polk, V. Kannappan, I. Harruna and P. Metha, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 931 (1986).
3. J. Walton and L. Phillip, Oxford Chemistry Primers, New York, p. 144 (2000).
4. T.S. Pradeesh, M.C. Sunny, H.K. Varma and P. Ramesh, *Bull. Mater. Sci.*, **28**, 383 (2005).
5. I. Issifu and B. Kofi, *Polym. Preprints*, **36**, 361 (1995).
6. N. Grassie, Chemistry of High Polymer Degradation Processes, Butterworth Scientific Publication, London, England, p. 118 (1956).
7. J. Watahabe, M. Hayashi, Y. Nakata, T. Niori and M. Tokita, *Prog. Polym. Sci.*, **22**, 1053 (1997).
8. C.K. Ober, J.I. Jin and R.W. Lenz, Liquid Crystal Polymers I, Advances in Polymer Science Series, Springer-verlag, New York, Vol. 59 (1984).
9. J. Watanabe, B.R. Harkness, M. Sone and H. Ichimura, *Macromolecules*, **27**, 507 (1994).
10. G. Elango, S. Guhanathan and T. Venkataraman, *Internat. J. Phys. Sci.*, **5**, 2104 (2010).
11. K. Kimura, S. Endo and Y. Kato, JP Patent 06080769 (1994).
12. Y. Mori, *Kogyo Zairyo*, **37**, 36 (1989).
13. H. Han and P.K. Bhowmik, *Prog. Polym. Sci.*, **22**, 1431 (1997).
14. J.R. Schaefgen, T.I. Bair, J.W. Ballou, S.L. Kwolek, P.W. Morgan, M. Panar and J. Zimmerman, in eds.: A. Ciferri and I.M. Ward, In Ultra-High Modulus Polym. (Lecture Seminar); Applied Science, Barking, England. p. 173 (1979).
15. W.-G. Kim and A.S. Hay, *J. Polym. Sci. A. Polym. Chem.*, **32**, 97 (1994).
16. J.J. Semler and J. Genzer, *J. Chem. Phys.*, **125**, 014902 (2006).
17. J.J. Semler, Y.K. Jhon, A. Tonelli, M. Beevers, R. Krishnamoorti and J. Genzer, *Adv. Mater.*, **19**, 2877 (2007).