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SYNTHESIS AND CHARACTERIZATION OF POLYGLYCERYL - TRIACRYLATE

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ABSTRACT

A high temperature polyester (polyglyceryl) triacrylate) have been synthesised by the esterfication of glycerol and acrylic acid followed by addition polymerization of glyceryl triacrylate in presence of benzoyl peroxide. The polyester is thermoset, solid very hard, completely insoluble in water and common organic solvents. The FTIR spectrum shows the presence of ester linkage. Differential scanning calorimeter shows that the polyester is thermally stable upto 350°C. A tentative structure of the polymer is proposed.

Key words: Polyglyceryl - triacrylate, esterfication, polymerization.

INTRODUCTION

In recent years, high temperature plastic are gaining industrial importance to variety of its applications. Several high temperature polyesters have been prepared[15]. Aliphatic polyester[6] has been prepared by poly condensation between the dicarboxylic acid and diols, but they have limited application due to its low melting points. This problem was overcome by introducing aromatic ring into the polyester chain. Polyester such as polyethylene terephthalate has high melting point and is commercially one of the most popular polyester marketed as terelene. This polyester is virtually unaffected by chemical and used as textile fiber[7]. It has a good mechanical strength upto 175°C. The. poly butylene terephthalate has been reported[8], which can stand upto 228°C. This polyester reinforced with glass fiber has been used to replace nylons and metals for application as gear parts and industrial machine. Hedric *et.aP.* have prepared a commercially useful nanofoams from aliphatic polyester-based copolymer. High temperature polyesters are industrially very interesting however, only a few reports are available. It seems interesting to synthesis new economic polyesters which can be mechanically stable to high temperature. In this communication, we are reporting poly glyceryl triacrylate, which is thermally stable upto 340°C.

EXPERIMENTAL

Glycerol(SRL), acrylic acid (SISCO), benzoylperoxide(CDH),

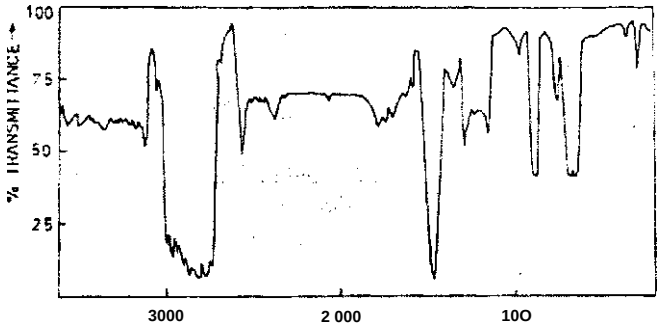

Figure 1 : FTIR Spectrum of polyglyceryl-triacrylate. Tolerance 20% in KBr.

dichloromethane(Qualigen), dicyclohexylc arbadimide and pyridine(Merck), sillica gel G, sodium bicarbonate(BDH), zinc powder (Nice) were used as such. Glyceryl-triacrylate was prepared in three step reaction. To acrylic acid in CCI_4, Br_2 was added drop wise in an ice bath with constant stirring. The resulting 2,3 dibromo acrylic acid was refluxed with glycerol and dicyclohexyl carbadimide in CCI_4 for 8 hours. The reaction mixture was then washed with water and sodium bicarbonate solution diluted with dichloromethane and filtered to separate dicyclohexyl urea m.p. 320°C. The filtrate was evaporated to remove dichloro methane and dicyclohexylcarbadimide to get glyceryl tri (2,3 dibromo propanoate) 80% b.p. 175°C. The later was denominated with Zinc dust at room temperature to yield glyceryl triacrylate 80%, $C_{12}H_{14}0_6$ (found C, 56.69%, H, 5.51%, O, 37.80%, required C 56.69%, H, 5.51%, O, 37.79%), V_{max} (KBr) 1744cm^{-1} (-COOC-),1146 cm^{-1}, 1188cm^{-1} & 1248cm^{-1}(-C-0-C-) 1631cm^{-1}, 934cm^{-1}, 896cm^{-1} (-C=C-).

Addition polymerzation was performed by heating glycerol- triacrylate with appropriate concentration of benzoyl peroxide in a closed vessel at 80°C and was purified in acelone. $C_{12}H_{14}0_6$ (found C, 56.7%, H5.51%, O, 37.80%, V_{max} (KBr) 1597cm^{-1}, (-COOC-) 1138cm^{-1}, 1248cm^{-1} (-C-0-C-) figure 1. Elemental analyzer (Heraeus Cairo Erba 1180) performed the elemental analysis of the monomer and polymer and bromine was estimated by fusion mixture method[10]. Purity of the compound was checked by thin layer chro-matography with silica gel Gas absorbent in toluene/methanol solvent system. The monomer do not possess usual test of -OH groups, and -COOH groups. On the other hand monomer consumes 2.8 moles of bromine confirming the presence of about three double bonds in the monomer.

Differential Scanning Calorimeter: Analysis:

A typical Differential scanning calorimeter (DSC) thermogram of polyglyceryl triacrylate at the rate of 20°C/ min. is shown in figure 2.The thermogram shows glass transition temperature at 90°C. On further heating an exothermic reaction appears but not prominent and the esier releases some heat of crystallization at 150°C, thereafter another endothermic peak at around 270°C, which correspond to the melting/ softing of unsaturated polyglyceryl-

triacrylate. Further system comes to the base line around 340°C and it shows a sharp endothermic peak beyond 400°C, which may be due to thermaly induced decomposition of polyglyceryl triacrylate.

RESULTS AND DISCUSSION

Glyceryl-triacrylate monomer (Containing three double bond) was synthesized by esterfication of glyeceryl' and 2,3- dibromo propanoic acid and further debromination of glyceryl tri (2,3 dibromo propanoate). The monomer is further subjected to addition polymerization in presence of free radical initiator benzoyl peroxide at 80°C. Polyester obtained was cured at 110°C.

Polyester obtained is very hard, tough, and yellpw colored solid. The polyester is insoluble in water , alcohol, ether, toluene, chloroform, CCl_4, dichloro methane, DMF, pyridine, THF, glacial acetic acid, and mineral acids. FTIR analysis shows the absence of hydroxyls groups and presence of ester linkage[11] (Figurel). DSC analysis shows that the polyester is stable upto 340°C Figure (2). A tentative structure of polyester is proposed (Figure 3). It appears that polyester is highly cross-linked and networked. This polyester is economic, easy to prepare, have good tensile strength and high melting point., therefore it appears that it is useful for wide industrial application.

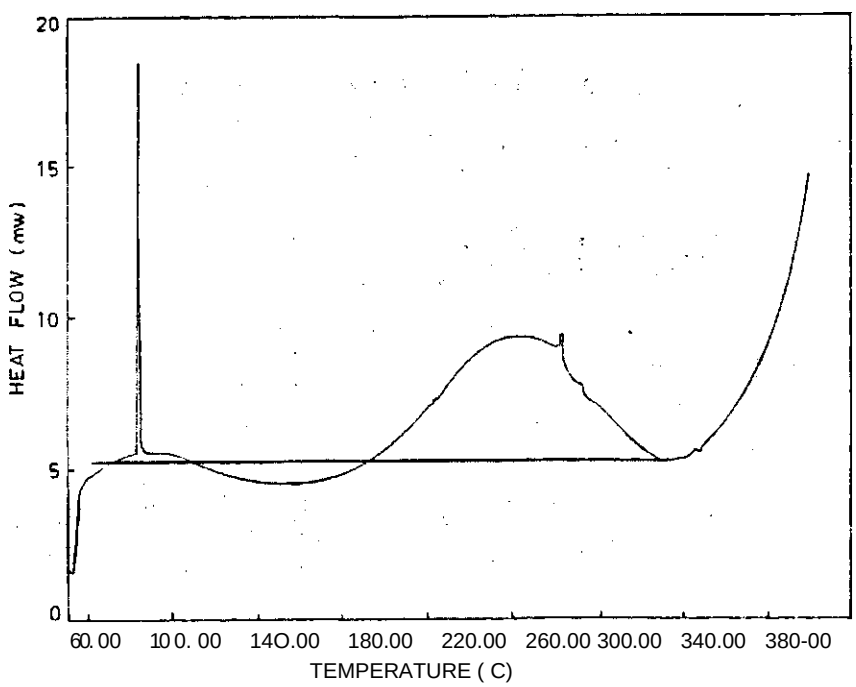

Figure 2: DSC thermogram of polyglyceryl triacrylate. Scanning rate 20°C/min. (Perkin-Elmer DSC-7)

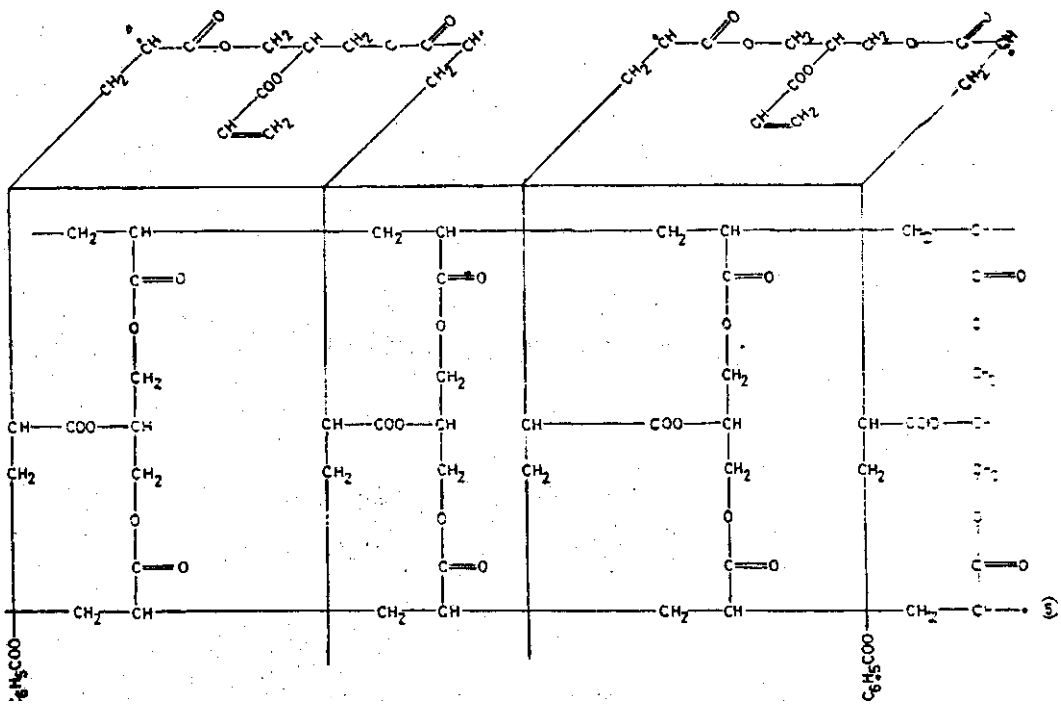

Figure 3: Structure of Polyglyceryl- triacrylate.

REFERENCES

1. Ellwood P., *Chem. Eng.,* **74,** 98(1967)

2. Witspiepe W.K., *Polym. PreprintsAZ,* 688(1972)

3. Assman K. & Schneider H.A., *Mol. Cryst. Lig. Cryst.'* **231,** 29(1993)

4. Eon J.W.L. & Whitten D.G., *Am. Chem. Soc,* **117,** 2226(1995)

5. Amouri I.El, Koulios A.S. & Quentin J.P., *Macromol. Chem. Phys.* **196,** 2081(1995)

6. Rodinguez F., *Principles of Polymer Systems,* 4 Ed. Taylor & Franches Publications, Chapter15, (1996)

7. Schildknecht C.E., Diallyl and related Polymers, in *Enc. Polym. Sci. Eng., 2* Ed., **4,** 779(1996)

8. Chern Y.T., Macromolecules, **28** 5561 (1995)

9. Hedrick J.L., Charter K.R., Richter R., Miller R.D., Russel TP, Flores V., Meccereyes D., Dubois Ph., and Jerome R., *Chem. Mater.A O ,* 39 (1998)

10. Turniss B.S., Hannaford A.J., Smith P.W.G., Tartchell A.R., *Vogel's Text Book of Practical Organic Chemistry* 5 *Ed.* Longman group U.K.Ltd. , pp 1224(1994)

11. Margareto Avram and Mateescu G.H.D., *Infrared Spectroscopy,* Rebert E. Krieger, Publishing Company, New York, , pp 420(1978)