

Synthesis and Characterization of Poly-1,3-dimethyloldiacrylate propane-2-ol and Its Use as Foam

PRAFULLA CHETRI, NEELOTPAL SEN SARMA and NARENDRA NATH DASS*
Material Sciences Division, Polymer Unit, IASST, Paschim Boragaon,
Garchuk, Guwahati-781 035, India
E-mail: narendas@sify.com

Poly-1,3-dimethyloldiacrylate propane-2-ol (P-DMDAP) was prepared by the homogeneous esterification of glycerol with acrylic acid. The formation of the ester was confirmed by the IR and ¹H NMR spectra. The polymer P-DMDAP shows appropriate foam character for laser target, if the density range lies 5-200 mg/cc. The pore size of the polymer was determined by SEM analysis. The thermal behaviours were studied by thermogravimetric analysis and differential thermogravimetric technique.

Key Words: Polyester, Foam, Homogeneous esterification, Pore size.

INTRODUCTION

In recent years synthesis of plastic foams has been attracting the attention of scientists of high-pressure and laser target laboratories. The desirable characteristics for such polymers are appropriate porosity, cohesive character, processibility and molecular weights. C, H, and N foams are also prepared for the development of ideal foam plastics¹. Since certain salts of poly-2-vinyl pyridine have good self adhesive properties to metals, they are also tried. Other potential candidates of polymeric foams are polystyrene, polyurethane, polyacrylate etc because they form foams with foam inducing agents.

Low-density foams can be potential candidates for producing a uniform energy deposition in direct drive in inertial confinement fusion (ICF) and enhancement of pressure. Plastic foams of density 30 to 200 mg/cc and thickness 60 μ appear to be useful for such experiment. The well-known monomer used for production of porous plastics *in situ* is trimethyl propane triacrylate (TMPTA)² with the formula (C₁₅H₂₀O₆)_n. In the present study 1,3-dimethylol diacrylate propane-2-ol (DMDAP) is used to produce polymeric foam, poly-DMDAP, which may be a potential candidate for the laser plasma experiments³⁻⁶. The foam was characterized by IR, ¹H NMR, TGA and SEM techniques. The density and pore size of the foam were also determined.

EXPERIMENTAL

Glycerol (Qualigen reagent grade) was used without further purification. Dimethyl formamide (BDH reagent grade) was purified by distillation under vacuum. Acrylic

acid (BDH reagent grade) was purified according to the procedure adopted by O'Neil⁷. Methanol (Qualigen reagent grade) and ethanol were used without any purification.

Preparation of P-DMDAP: The polymer P-DMDAP is synthesized from the glycerol and acrylic acid. 2.5 mL of glycerol and 0.5 mL of acrylic acid (1:1 mol) are esterified in presence of few drops of sulfuric acid. Homogeneous esterification was carried out by heating the reaction mixture, for about 48 h at a temperature around 60 °C. The water produced during the reaction was removed from the reaction medium as and when it was formed by the Dean and Stark principle⁸. After completion of the reaction the solvent was removed by distilling under vacuum. The polymer was separated from the monomer first with the help of methanol and then with water. The polymer was then dissolved in water and recrystallized with methanol.

The ester so formed was dissolved with DMF, sprayed on glass plate and aluminum foil of thickness 5-10 μ and dried at room temperature. Ethanol was then sprayed over the dried polymer and allowed to dry for 0.5 h when the polymer shows the foam like appearance. This technique is useful to produce foams in the required position in the target without any machining or handling, thereby reducing the risk of damage to the foam.

The foams reported here are of fine-structured glycerol acrylate with submicron pore diameter. The IR of the P-DMDAP was recorded in the region between 4000 and 200 cm^{-1} with a Perkin-Elmer spectrophotometer using KBr technique. The proton NMR was recorded with a WH-270 NMR spectrometer. The spectrum was obtained on solution containing P-DMDAP in DMSO with tetramethylethylsilane as an internal reference. TGA and DTG were performed using Mettler Toledo Star thermal analyzer in air at a heating rate of 10 °C/min using 5 ± 1 mg samples. The particle size of the P-DMDAP was measured with the help of scanning electron microscope (Model LEO 1430VP). The uniformity of the pore size was observed by LEICA WILD MPS 52 phase contrast microscope.

RESULTS AND DISCUSSION

IR spectrum of P-DMDAP shows a strong band at 1739 cm^{-1} due to the C=O group⁹ which confirmed the formation of the ester. A medium band also appeared at 1628 cm^{-1} for the C=C. Asymmetric and symmetric C-O-C stretching vibration appeared at 1263 and 1108 cm^{-1} , respectively. A broad band was observed at 3430 cm^{-1} due to an unreacted O-H group.

In a typical ¹H NMR spectrum of P-DMDAP. The signals observed at 2.4-2.6 and 3.2-3.7 ppm are due to methylene (-CH₂-) and methine (>CH-) proton, respectively¹⁰. The signal at 2.88 ppm is due to unreacted hydroxyl group (-OH)¹¹.

To check the thermal stability of P-DMDAP the TGA and DTG curves (Fig. 1) were recorded in air. From DTG curves, it was observed that P-DMDAP decomposed in three stages. The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the TGA curve with its base-line. The first

stage degradation was due to removal of H₂O from the unconverted hydroxyl groups as well as due to cleavage of the ester groups of the P-DMDAP¹². The initial decomposition temperature (IDT₁) for first stage of the P-DMDAP was 210 °C. The second stage decomposition was due to the removal of CO, CO₂, hydrocarbons, *etc.*¹³ from the PDMDAP. The initial decomposition temperature (IDT₂) for the second stage of the PDMDAP was 315 °C. The third stage decomposition was due to the production of carbon at temperature above 400 °C. Integral procedural decomposition temperature (IPDT)¹⁴ was found to be 285 °C.

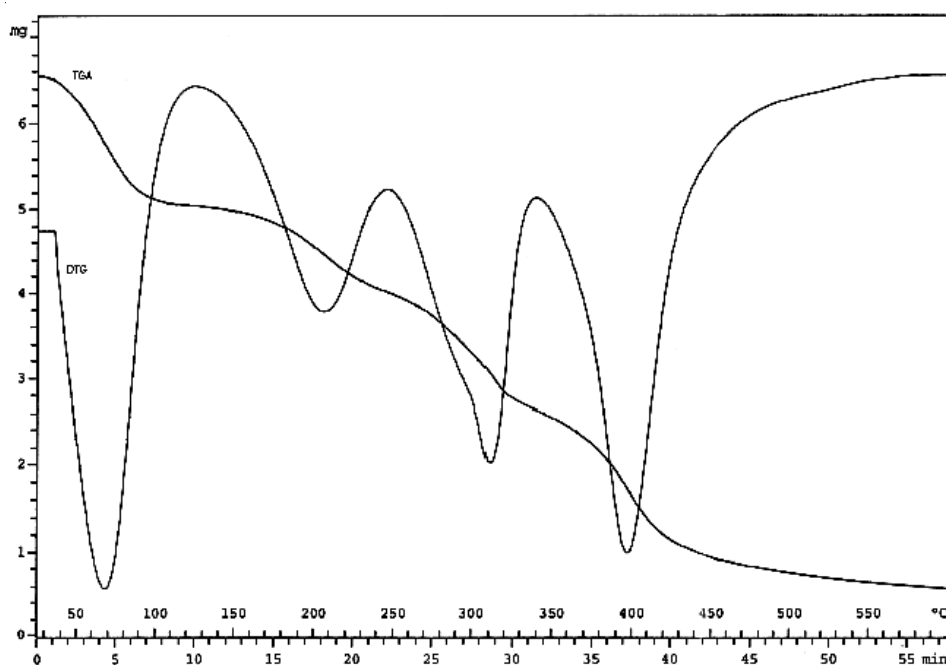


Fig. 1. TGA and DTA of P-DMDAP

To check the uniformity of the pore, a small amount of the polymer was transferred onto a glass slide of 0.3 mm thickness and it was analyzed with the help of LEICA WILD MPS 52 phase contrast microscope¹⁵. The image gives the number of pores per unit volume of the foam. SEM clearly demonstrates the optical transparency, the uniformity and spherical character of the foam. The analysis of the SEM indicates that the density of the foam is uniform throughout and that the foam shows the same submicron cell structure.

The SEM of the foam P-DMDAP shows various closed and open cells (Fig. 2a and 2b). The densities and pore sizes of the polymer on aluminum foil of different thickness are given in Table-1. The table shows that the density decreases with the rise of pore size.

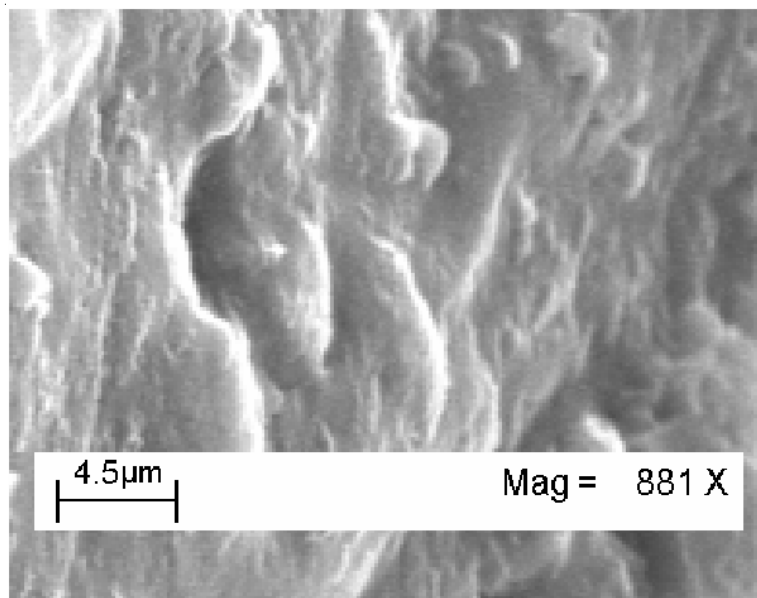


Fig. 2a. Scanning electron micrograph of P-DMDAP

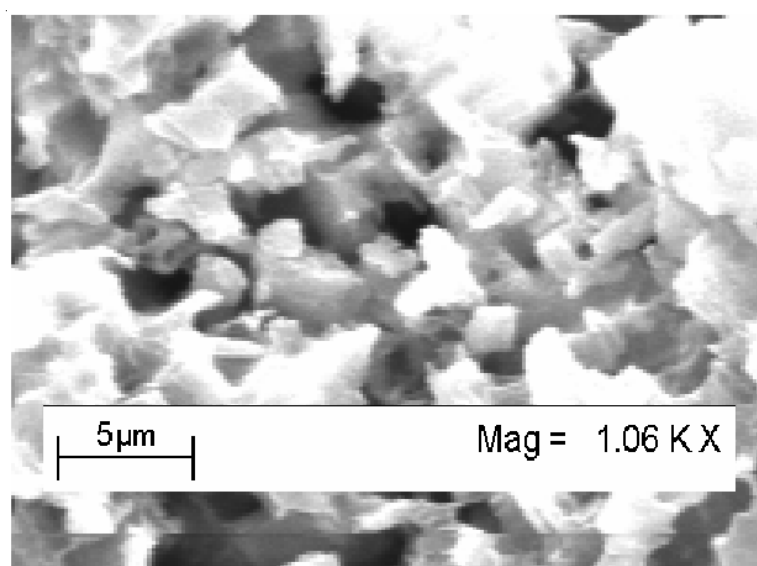


Fig. 2b. Scanning electron micrograph of P-DMDAP foam

TABLE-1
DENSITIES AND PORE SIZES OF THE P-DMDAP FOAM

Samples	Density (mg/cc)	Pore size (μ)
5 μ Al foil	81.59	32.0
10 μ Al foil	51.67	45.0

Conclusion

The foam of P-DMDAP is known to be used as a pressure application material in laser experiment. However, the preparation is obscurely defined in literature. The control of various parameters like porosity, density, adhesive character are very vital for technical use of these of high valued materials. The P-DMDAP foam prepared in our laboratory has similar properties and so the foam is sent to Bhabha Atomic Research Centre, Mumbai for further investigation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from DAE, Government of India.

REFERENCES

1. P. Chetri, N.N. Dass and N. Sen Sarma, *Mater. Sci. Eng.*, **B128**, 188 (2006).
2. W. Nazarov, *J. Moscow Phys. Soc.*, **8**, 251 (1998).
3. D. Batani, W. Nazarov, T. Hall, T. Lower, M. Koenig, B. Faral, A.B. Mounaix and N. Grandjouan, *Phys. Rev. E*, **62**, 8573 (2000).
4. R. Aveyard, B.P. Binks, P.D.I. Fletcher, T.G. Peck and C.E. Rutherford, *Adv. Colloid. Interface Sci.*, **48**, 93 (1994).
5. R.J. Pugh, *Adv. Colloid Interface Sci.*, **64**, 67 (1996).
6. J.F. Sadoc and N. Rivier, *Foams and Emulsions*, Kluwer Academic, Dordrecht, p. 354 (1999).
7. T. O'Neil, *J. Polym. Sci.*, **A110**, 569 (1972).
8. N. Macmillan, *An Advanced Organic Laboratory Course*, Longmans, New York, p. 10 (1972).
9. P. Chetri, N.N. Dass and N. Sen Sarma, *J. Polym. Mater.*, **23**, 55 (2006).
10. P. Chetri, N.N. Dass and N. Sen Sarma, *J. Appl. Polym. Sci.*, **102**, 5675 (2006).
11. P. Chetri, N.N. Dass and N. Sen Sarma, *Mater. Sci. Eng.*, **B139**, 261 (2007).
12. P. Chetri, N.N. Dass and N. Sen Sarma, *Pol. Bull.*, **58**, 489 (2007).
13. P. Chetri and N.N. Dass, *J. Appl. Polym. Sci.*, **81**, 1182 (2001).
14. C.D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
15. N.N. Dass, P. Chetri, H. Das and N. Sen Sarma, *J. Polym. Mater.*, **24**, 49 (2007).

(Received: 1 August 2008;

Accepted: 25 March 2009)

AJC-7372