

Mercaptoacids initiated ring opening polymerization of ϵ -caprolactone

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ABSTRACT: Ring opening polymerization (ROP) of ϵ -caprolactone (CL) was carried out at 160°C under nitrogen atmosphere by using two different mercaptoacid as individual initiators such as mercaptosuccinicacid (MSA) and mercaptoaceticacid (MAA) by bulk polymerization method. The initiating efficiency of initiator was confirmed by the % yield of poly (ϵ -caprolactone) (PCL) formed. Thus obtained PCL was characterized by fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The results are critically analyzed and compared with the literature.

Keywords: Ring opening polymerization, mercaptoacids, poly (caprolactone) synthesis, characterization

INTRODUCTION

PCL has recently received great attention because of their tunable thermal properties and bio-degradability leading to various bio-medical applications. Such a bio-medical polymer can be synthesized by the ROP process in the presence of an initiator and a catalyst. Rare earth catalyzed ROP of CL was done by Oshimura et al (Oshimura et al., 2010). Dioxomolybdenum complexes were examined as a catalyst for the ROP of CL (Maruta et al., 2014). In 2014, Degirmenci and research team (Degirmenci et al., 2014) reported about the mid-chain macrophotoinitiated PCL. Diphenylzinc initiator was used for the ROP of CL (Contreras et al., 2014). Recently, our research team has used different initiators for the ROP of CL (Meenarathi et al., 2015, Kannammal et al., 2014, Agathian et al., 2013, Sribala et al., 2013). A novel Schiff base as an initiator for the ROP of CL was reported in the literature (Sowkath et al., 2014). Qiu et al (Qiu et al., 2007) studied the PEI initiated ROP of CL. Recently, Sivabalan and co-workers (Sivabalan et al., 2014) used different initiators for the ROP of CL. By thorough literature survey, we found few reports are available based on the mercaptoacid initiated ROP of CL. This urged us to do the present investigations by considering two different

mercaptoacid as an individual initiator for the ROP of CL.

EXPERIMENTAL

Materials

ϵ -caprolactone (CL, Aldrich, India), Stannous octoate (SO, Aldrich), mercaptosuccinicacid (MSA, Fine chemicals, India), mercaptoaceticacid (MAA) and CHCl_3 were purchased from Spectrum, India. Diethyl ether (CDH, India) was purchased and used as received. Double distilled (DD) water was used for washing purpose.

Synthesis of PCL by using MSA or MAA as an initiator

Required amount of ϵ -CL monomer was charged in a 25 mL RB flask. 0.10 g MSA or MAA initiator was added. 0.001 g of S.O catalyst was also added. The $[M/I]=10$ and $[M/C]=1000$. The reactants are thoroughly mixed well under N_2 atmosphere for 10 min at room temperature. The temperature of the reaction was raised to 160°C, now the ROP of ϵ -CL has been started. After 2 hrs, the RB flask was removed from the oil bath and cooled. The product was further purified by adding 10 mL of CHCl_3 solvent and re-precipitated by the addition of 200 mL

diethyl ether. The contents were dried under fume hood. Thus obtained white precipitate is MSA or MAA end capped PCL. The product was weighed and stored in a zipper lock cover. Further, the ROP of ϵ -CL was checked by various analytical techniques.

Characterization

DSC and TGA were measured by using Universal V4.4A TA Instruments (simultaneous DSC and TGA analyzer) under nitrogen atmosphere at the heating rate of 10 K/min from room temperature to 373K. FTIR spectrum was taken by using Shimadzu 8400 S, Japan model instrument from 4000-400 cm^{-1} by KBr pelletisation method. Surface morphology of the sample was measured by JSM 6300, Jeol product, SEM instrument.

RESULTS AND DISCUSSION

The initiating efficiency of the initiator can be compared based on the % yield of the polymer obtained. The % yield was calculated to be 97.8 and 99.3% corresponding to the MSA and MAA initiator. This confirmed that the MAA is a good initiator for the ROP of CL than the MSA initiator.

Figure 1 indicates the FTIR spectra of polymer synthesized by two different initiators. Figure 1a represents the FTIR spectrum of PCL synthesized by using MSA as a chemical initiator. A broad peak around 3443 cm^{-1} explained the -OH ended PCL chains. The C-H symmetric (2863 cm^{-1}), antisymmetric (2942 cm^{-1}), C=O (1726 cm^{-1}), C-O-C ester linkage (1186 cm^{-1}) and C-H out of plane bending vibration (730 cm^{-1}) were observed corresponding to the PCL backbone. A peak at 1362 cm^{-1} accounted the C-S stretching, appeared from the MSA. Figure 1b indicates the FTIR spectrum of MAA end capped PCL chains. Here also one can observe the above said peaks. In 2015, Meenarathi and research team (Meenarathi et al., 2015) narrated the FTIR spectrum of PCL.

The melting temperature T_m of PCL was determined by DSC method. Figure 2a represents the DSC thermogram of PCL-MSA system. The thermogram exhibited an endothermic peak corresponding to the T_m of PCL at 55.2°C. The DSC heating scan of PCL-MAA system is shown in Fig. 2b with a T_m value of

56.8°C. In comparison, the former system exhibited lower T_m due to the hydrophilic nature of the initiator. This leads to the absorption of moisture and hence decrease of T_m . Recently, Sivabalan et al (Sivabalan et al., 2014) explained the DSC of PCL synthesized by different chemical initiators. Our DSC results are co-inside with the literature.

The thermal stability of PCL was investigated by TGA method. As shown in Fig. 3a, the TGA thermogram exhibited a two-step degradation process for PCL-MSA system. Up to 200°C there is no weight loss, this confirmed the hydrophobic nature of PCL. The first minor weight loss around 290°C is due to the breaking of interaction between MSA and PCL chain. The second major weight loss around 400°C is ascribed to the degradation of PCL backbone. This is in accordance with Meenarathi et al (Meenarathi et al., 2015) report. The TGA thermogram of PCL-MAA system is shown in Fig. 3b with two step degradation process. The first and second weight loss steps are corresponding to the PCL-MAA linkage degradation and PCL backbone degradation respectively. In overall comparison, the PCL-MAA system showed higher % weight residue at 292°C, corresponding to the degradation of PCL-MAA linkage. The degradation temperature of PCL is in accordance with the reported literature (Sivabalan et al, 2014).

The surface morphology of PCL synthesized by two different chemical initiators is reported in Fig. 4. Figure 4a is corresponding to the SEM image of PCL-MSA system. Broken stone like morphology with some voids are seen in the image. This is a typical surface morphology of PCL (Meenarathi et al., 2015). Figure 4b denotes the surface morphology of PCL-MAA system. Here also one can see the above said surface morphology. The surface morphology study indicates that the surface morphology of a polymer cannot be varied that much by the initiator.

CONCLUSIONS

The following niche points are presented here as conclusion. The ROP of CL was carried out

successfully through bulk polymerization method by using two different initiators. The MAA initiator exhibited higher % yield than the MSA system. The FTIR spectrum declared the presence of stretching corresponding to the initiators (C-S stretching). The DSC and TGA studies confirmed and informed that the MAA initiated system exhibited higher thermal properties. The surface morphology of PCL was found to be the same for both the MAA and MSA systems.

REFERENCES

- Oshimura, M., Takasu, A. 2010. Controlled ring opening polymerization of caprolactone catalyzed by rare earth perfluoroalkanesulfonate and perfluoroalkanesulphonimides. *Macromolecules*, 43: 2283-2290.
- Maruta, Y., Abiko, A. 2014. Random copolymerization of caprolactone and lactide with molybdenum complexes. *Polym. Bull.*, 71: 989-999.
- Degirmenci, M., Sarac, M.A., Genli, N. 2014. Synthesis and characterization of midchain microphotoniator of poly(caprolactone) by combination of ring opening polymerization and click chemistry. *Polym. Bull.*, 71: 1743-1755.
- Contreras, J., Pestana, J., Carrasqueno, F.L, Torres, L. 2014. Synthesis of caprolactone-b-lactide blocks copolymers by mean sequential polymerization using diphenyl zinc as initiator. *Polym. Bull.*, 71: 1661-1674.
- Meenarathi, B., Palanikumar, S., Kannammal, L., Anbarasan, R. 2015. Synthesis, characterization and catalytic activity of Ag-acidfuchsin nanohybrid system towards ring opening polymerization of caprolactone. *Spectrochim.Acta Part A*, 135: 93-100.
- Kannammal, L., Meenarathi, B., Palanikumar, S., Yelilarasi, A., Anbarasan, R. 2014. Synthesis, characterization and band gap energy of poly(ϵ -caprolactone)/Sr-MSA nano composite. *J. Phys. D. Appl. Phys.*, 47: 1-10.
- Agathian, K., Siva, P., Kannammal, L., Meenarathi, B., Anbarasan, R. 2013. Luminol initiated ring opening polymerization of ϵ -caprolactone. *Ind. J. Sci.*, 5: 37-40.
- Sribala, M.G., Chen, H.H., Chen, P.H., Meenarathi, B., Kannammal, L., Siva, P., Anbarasan, R. 2013. Synthesis and characterizations of poly (ϵ -caprolactone) based hydrophobic copolymers. *Ind. J. Sci.*, 5: 41-48.
- Sowkath, A., Mansoor A., Anbarasan, R. 2014. Ring opening polymerization of ϵ -caprolactone by Schiff base metal complex. *Int. J. Chem. Bio. Sci.*, 1: 1-10.
- Qiu, L.Y., Bae, Y.H. 2007. Self assembled PEI-grafted poly(caprolactone) micelles as potential dual carriers of genes and anticancer drugs. *Biomaterials.*, 28: 4132-4142.
- Sivabalan, A., Hariharasubramani, R., Palanikumar, S., Meenarathi, B., Anbarasan R. 2014. Synthesis and characterization of poly(ϵ -caprolactone): A comparative study. *Int. J. Sci. Res. Eng. Tech.* 1: 9-15.

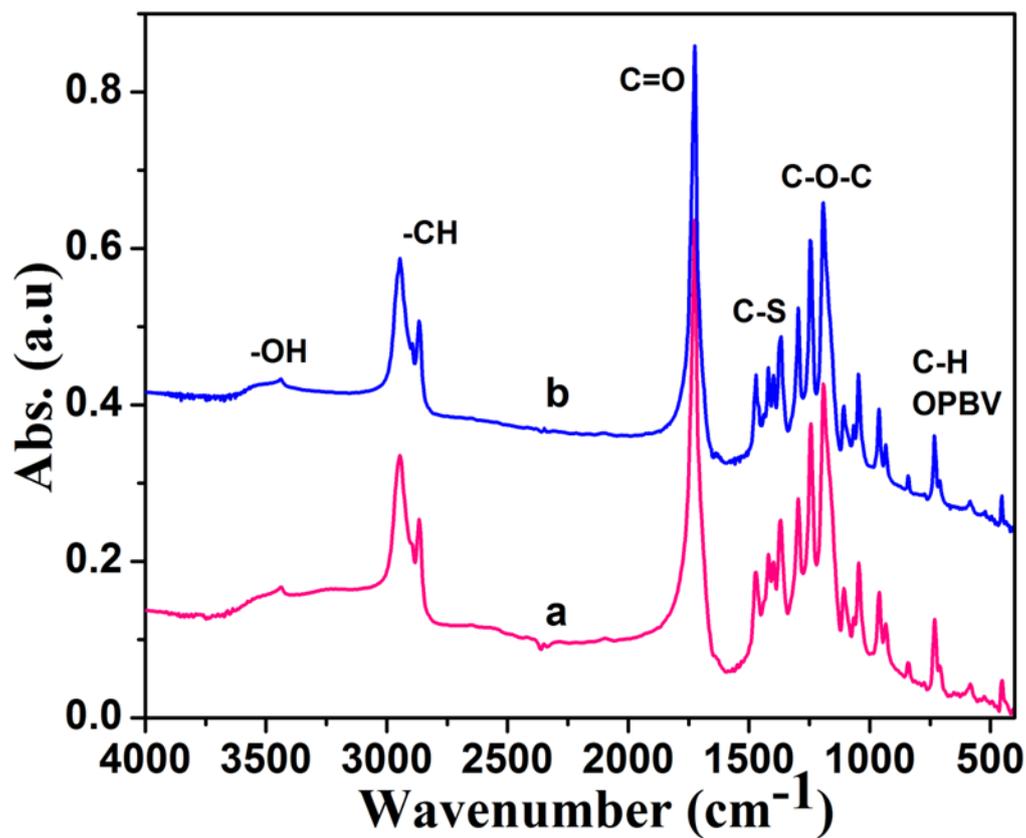


Figure 1 FTIR spectrum of (a) PCL-MSA, (b) PCL-MAA systems

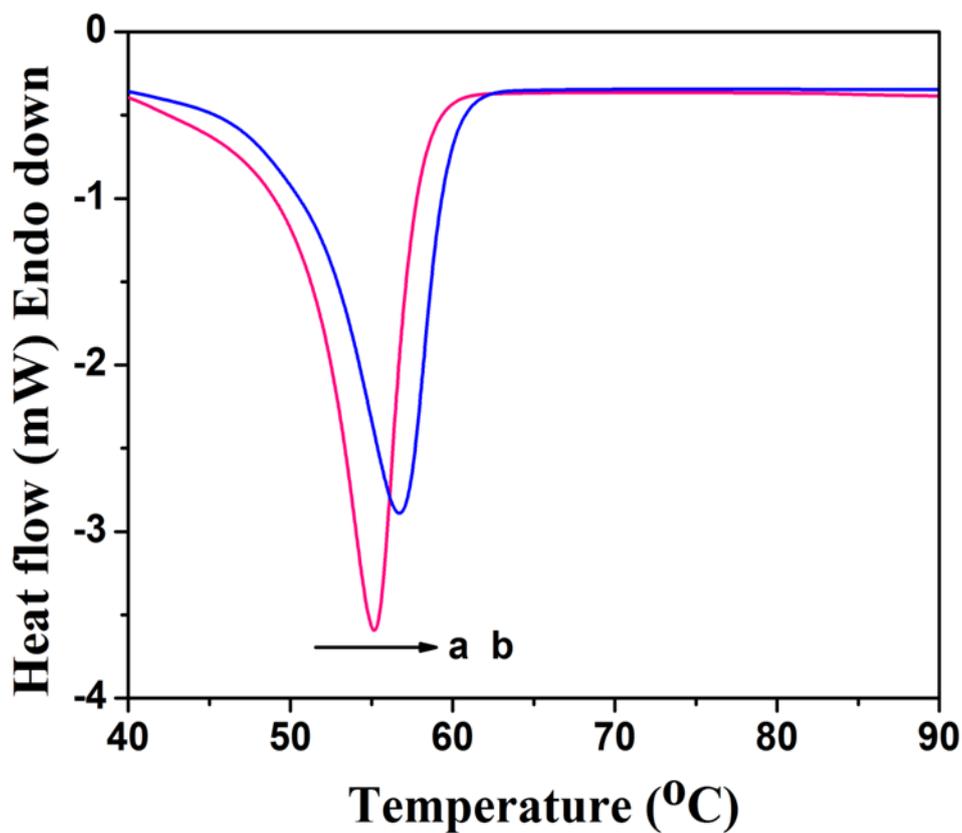


Figure 2 DSC thermogram of (a) PCL-MSA, (b) PCL-MAA systems

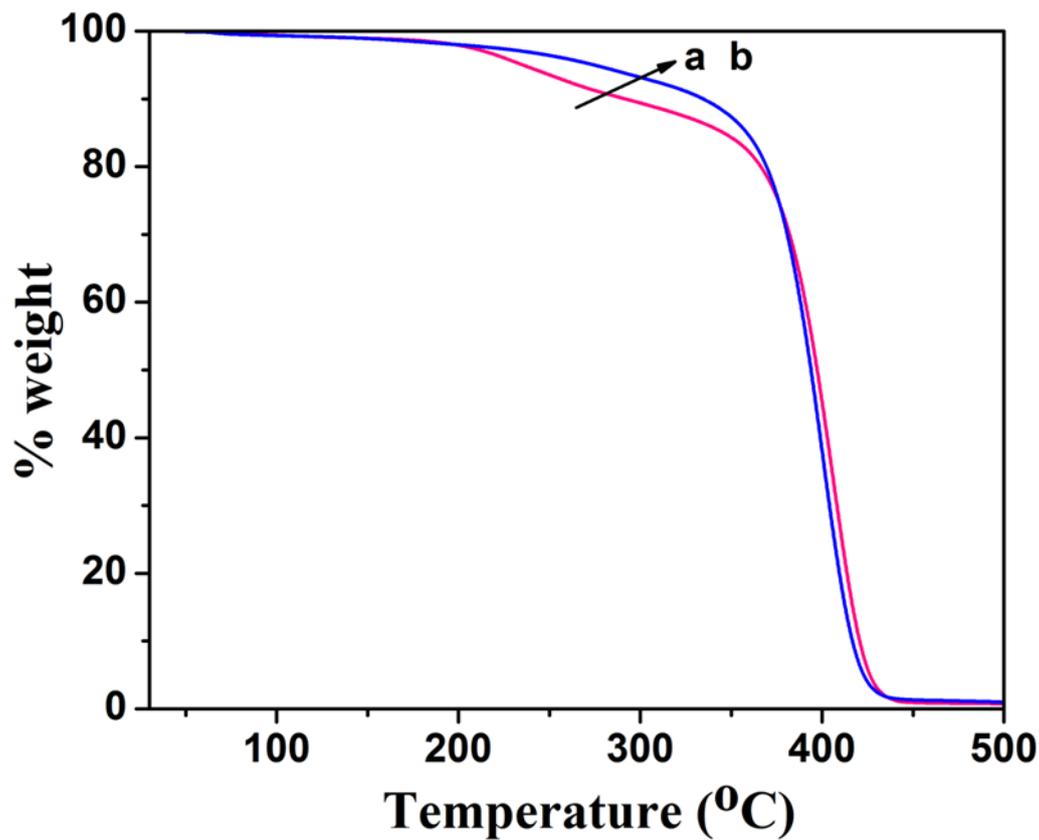


Figure 3 TGA thermogram of (a) PCL-MSA, (b) PCL-MAA systems

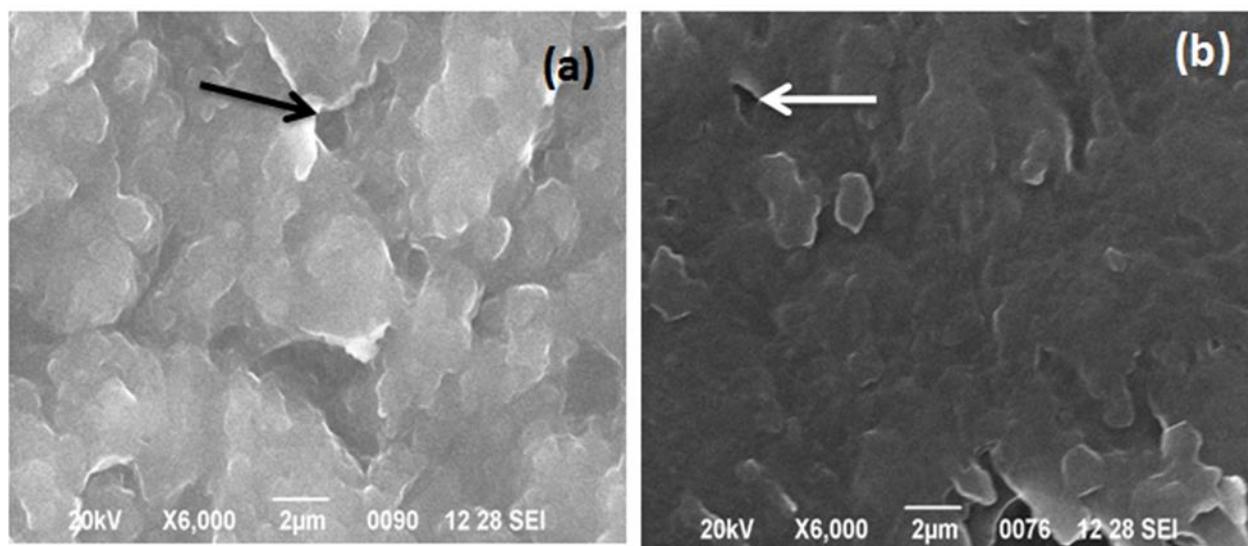


Figure 4 SEM image of (a) PCL-MSA, (b) PCL-MAA systems