J. Chem. Research (S), 1999, 452–453†

Effect of Dimethylformamide on the Ring Opening Insertion Polymerization of ϵ-Caprolactone†

Alexander Kavros, Yashica L. Robinson and Stephen Rimmer*

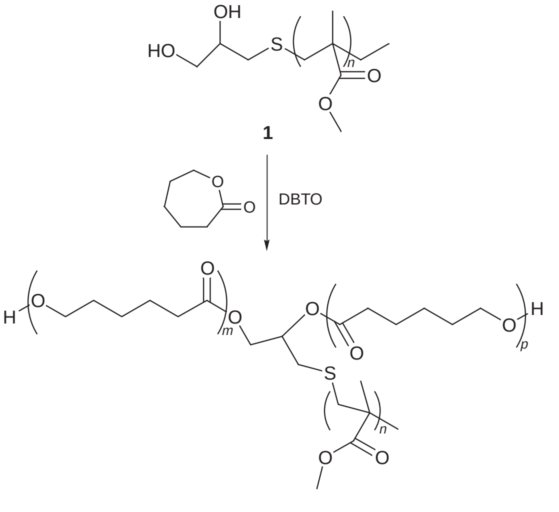
The Polymer Centre, Lancaster University, Lancaster LA1 4YA, UK

Ring-opening insertion polymerization of ϵ-caprolactone is retarded in dimethylformamide when catalysts such as dibutyl tin oxide, zinc acetate and titanium tetrabutoxide are employed.

Poly(ϵ-caprolactone) (PCL) is a well-known biodegradable polyester that can be prepared by the ring-opening insertion polymerization of ϵ-caprolactone (CL). Its molecular weight can be controlled by the addition of low molecular weight alcohols.[1] In this case transfer to the alcohol yields a polymer with a hydroxy functionality at the α end and a functionality derived from the alkoxy moiety at the ω end. This type of methodology has been used to produce a wide range of oligomers and functional polymers. During our work on this polymerization methodology[2–5] we have noticed that the amide solvent dimethylformamide (DMF) has a deleterious effect on the course of the polymerization. We here present the results of our observations and postulate that the effect is due to an unfavourable interaction between the amide group and the metal catalyst.

Results and discussion

Polymerizations Involving Chain Transfer to PMMA Diol.—Our initial interest in the effect of DMF on this polymerization was based on the observation that the polymerization in the presence of compound **1** is retarded by DMF. Ring-opening polymerization of CL in the presence of **1** yielded an oligo(ϵ-caprolactone-*graft*-methyl methacrylate) diol as shown in Scheme 1.



Scheme 1 Synthesis of a poly(ϵ-caprolactone-*graft*-methyl methacrylate) *via* polymerization of CL with transfer to compound **1**

Several reactions were performed in various solvents and in the presence of compound **1** as shown in Table 1.

Surprisingly the catalysed polymerization in DMF has a lower rate than even the non-catalysed polymerization in chlorobenzene. We first considered that the solvent polarity may play a role. Therefore, the reaction was carried out in a series of solvents of widely differing relative permittivity (ϵ). As can be seen from Table 1, the polarity of the medium does affect the reaction rate so that increasing ϵ tends to lower the rate of polymerization. However, the effect is quite small over the reaction times studied in this work. DMF also does not fit into the pattern because use of DMSO ($\epsilon = 46.6$) leads to a considerably higher rate of polymerization than DMF which is the less polar solvent of the pair ($\epsilon = 36.7$).

Polymerizations Involving Chain Transfer to Low Molecular Weight Diols.—Next polymerizations were carried out in the presence of two low molecular weight diols and three different catalysts. In order to mimic the end group structure of the PMMA diol each diol contained both primary and secondary hydroxy functionalities. The results are shown in Table 2.

Clearly here also a large decrease in the final conversion of CL was observed on changing the solvent to DMF. In each of the examples in Table 2 both the final degrees of polymerization and final conversion are lower when DMF is used as the solvent. Williams[7] has reported that metal catalysts such as DBTO (dibutyltin oxide) react with DMF. From the results reported here it would appear that in the insertion polymerization of CL this DMF/catalyst interaction is effectively a catalyst-poisoning step. DMSO

Table 1 Conversion of CL at 120 °C in various solvents; ϵ = relative permittivity of the solvent (taken from ref. 6)

Solvent	DBTO concentration/ (mmol dm^{-1})	Conversion of CL (mol %)	ε
Chlorobenzene	0.00	21	5.621
Chlorobenzene	5.5	100	5.621
Cyclohexanone	5.5	86	18.3
DMF	5.5	14	36.710
Dimethyl sulfoxide	5.5	78	46.600

Table 2 Comparison of the CL polymerizations carried out in DMF or xylene with low molecular weight diols

Solvent	Diol	Catalyst	Conversion (mol %)	Degree of polymerization (^{1}H NMR)
Xylene	PD	DBTO	97	6.9
DMF	PD	DBTO	50	4.9
Xylene	BD	DBTO	89	12.0
DMF	BD	DBTO	30	4.6
Xylene	BD	TBO	100	12.1
DMF	BD	TBO	6	3.4
Xylene	BD	Zn(OAc)$_2$	93	10.7
DMF	BD	Zn(OAc)$_2$	6	3.7

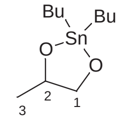
---

*To receive any correspondence (*e-mail*: s.rimmer@lancaster.ac.uk).

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

is also reported to react with DBTO[8] but this does not appear to have a detrimental effect on the polymerization (see Table 1).

Next we investigated the effect of DMF on some other well known CL polymerization catalysts. As can be observed from Table 2 similar results were observed when xylene was replaced with DMF. That is there was a severe retardation in the rate of polymerization and a sharp decrease in the final degree of polymerization. Thus we have shown that the retardation of the polymerization of CL by DMF is a general phenomenon. We considered that this retardation is probably due to catalyst poisoning involving preferential coordination of DMF to the metal centre. This hypothesis is supported by reference to the ^{1}H NMR spectra of the reaction products of equimolar quantities of propane-1,2-diol (PD) with DBTO in either DMF or xylene. In the case of the reaction carried out in xylene peaks due to PD (δ1.15, d, 3H; 3.36 and 3.55, m, 2H; 3.86, m, 1H; 4.6, d, 1H; 4.65, t) were absent from the spectra of the reaction mixture. Peaks at δ 1.12 ($2 \times$ d, 3H), 3.57 (m, 2H) and 3.7 (s, 1H) were observed. These resonances are due to protons 1–3 shown in **2**. When the reaction was carried out in DMF however resonances due to PD that was not co-ordinated to tin were observed. The amount of non-reacted PD amounted to 95% of that added to the reaction vessel. Thus it appears that retardation of the oligomerization reaction is due to an unfavourable interaction of DMF with the catalyst that prevents the formation of initiating species such as **2**.



2

Fig. 1 Probable structure of the organotin compound formed upon the reaction of DBTO with PD in xylene

Experimental

Preparation of Poly(methyl methacrylate) Diol **1**.—The methodology of Chujo *et al.*[9] exploited in our previous work[2] was used to prepare a PMMA diol **1** of molecular weight 850 g mol^{-1} (obtained from end-group analysis[2]).

Polymerization of CL in the Presence of Diols.—Compound **1** (10.00 g) was dissolved in CL (10.00 g). This stock solution was then split into fractions (1.0 g) and diluted with the appropriate solvent (4.0 g) as stated in Table 1. The indicated amount of dibutyltin oxide was then added and the mixtures heated for 49 h at 120 °C. The solvents were then removed by rotary evaporation and ^{1}1H NMR spectra (CDCl$_3$, 400 MHz, JEOL GX400) were recorded. The degree of conversion was calculated from the ratio of the oxymethylene protons, arising from the CL residues (δ4.06), to the backbone methylene protons arising from the MMA residues (δ1.8–2.1). Similar reactions were carried out with propane-1,2-diol and butane-1,3-diol (BD) and with the catalysts: DBTO, titanium tetrabutoxide (TBO) or zinc diacetate, Zn(OAc)$_2$. The catalyst concentration was 83 mmol dm^{-3} while the diol and CL concentrations were 0.4 and 4.6 mol dm^{-3} respectively. These reactions were conducted for 6 h.

Reaction of Equimolar Quantities of PD with DBTO in Xylene or DMF.—Equimolar amounts of PD with DBTO were dissolved in 5 ml of DMF or xylene. The concentration of both the catalyst and diol used was 2.60 mmol. Each reaction was conducted at 120 °C for 6 h, under a positive pressure of nitrogen. Continuous stirring was ensured throughout the reactions, enabling complete mixing of the reactants.

Received, 8th October 1998; Accepted, 6th April 1999
Paper E/8/07834C

References

1 A. Duda, *Macromolecules*, 1994, **27**, 576.
2 S. Rimmer and M. H. George, *Eur. Polym. J.*, 1993, **29**, 205.
3 S. Rimmer and M. H. George, *Polymer*, 1994, **35**, 2123.
4 S. Rimmer and M. H. George, *J. Macromol. Sci., Pure Appl. Chem.*, 1994, **A31**, 857.
5 S. Rimmer and M. H. George, *Polymer Commun.*, 1994, **35**, 5782.
6 *Handbook of Chemistry and Physics*, ed. R. C. West and M. J. Astle, CRC Press, Boca Raton, FL, 60th edn., 1980.
7 D. Williams, *Br. Pat.*, 1 008 002, 1996.
8 J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.*, 1967, **29**, 393.
9 Y. Chujo, T. Tasuda and Y. Yamashita, *Polym. Bull.*, 1981, **5**, 361.