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Phase transfer catalysis in the polycondensation processes

IV. Synthesis of polyesters with oxetane pendant groups

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Summary

Polyesters from 3,3'-bis(chloromethyl)oxacyclobutane and dipotassium isophthalate were obtained by phase transfer catalysis using different catalysts and solvents.The products were characterised by IR, ^{1}H-NMR and DSC.

Introduction

Phase transfer catalysis (PTC) has been widely used in synthesis of poly- and copolyethers [1-4],polycarbonates [5], polythiocarbonates[6,7],polythioethers[8,9],polyarilates[10] but less has been published on the synthesis of polyesters from dihalocompounds and alkali metal salts of dicarboxylic acids [11,12].

In this paper we report the synthesis of polyesthers with oxetane pendant group from 3,3'-bis(chloromethyl)oxacyclobutane (BCMO) and potassium isophthalate,using several catalysts and solvents under PTC conditions.

Experimental Part

Materials: 3,3'-bis(chloromethyl)oxacyclobutane was obtained as described in [3].Solvents and reagents were purchased from Fluka A.G. and Merck and were used as delivered. Dipotassium isophthalate was obtained from isophthalic acid by titration with solution in water of potassium hydroxide.

The following catalysts were used:TEBA-triethylbenzylammonium chloride;TMAC-tetramethylammonium chloride;MTPP-methyltriphenilphosphonium chloride and CPyAB cetylpyridylammonium bromide.

In a typical polycondensation reaction 5 mmoles of dipotassium isophthalate and 2 mmoles of catalyst dissolved in 20 ml of DMSO(or DMF) were mixed with 5 mmoles of BCMO. The mixture was stirred at 80°C for 8 hours, cooled and poured into a twofold excess of methanol.The precipitated polymer was filtered,washed with water to remove inorganic salts and methanol,then dried under vacuum at 40°C.

The IR spectra of the products (KBr pellets) were recorded on a Karl-Zeiss Jena UR-20 spectrophotometer.

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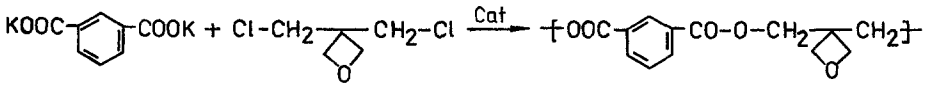
^{1}H-NMR spectra were run on a JEOL 60 MHz apparatus (DMSO-d6 solution).Thermal properties were evaluated by thermogravimetry on a PAULIK-PAULIK-ERDEY MOM thermobalance,at a heating rate of 10°C/min in air and by differential scaning calorimetry on a DuPont 2000 DSC-V4 equipment.

Results and Discussion

The poly-isophthalate was obtained according the following reaction:



The white powdered polymer resembled to the structure of corresponding substrates, i.e. isophthalate and BCMO.This is confirmed by the results of IR-and ^{1}H-NMR spectroscopic studies of the polycondensation products.In the IR- spectrum of the polyester is observed an absorbtion band at 1740 cm^{-1}, characteristic for C=O band in ester group, together with specific bands for aromatic (1490 and 1600 cm^{-1}) and oxetane rings(940 cm^{-1})Fig.1. For comparation the IR spectrum of BCMO is presented.

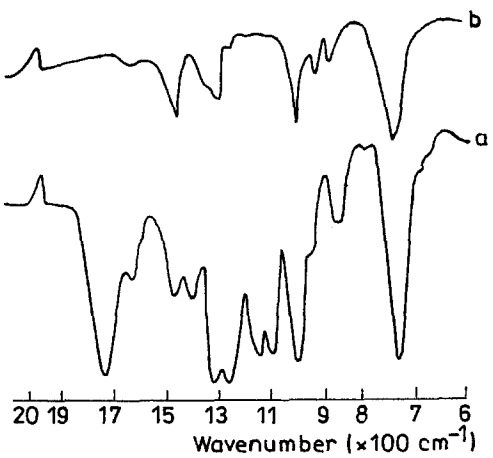


Fig.1 IR-spectra of the polyester (a) and BCMO (b)

The ^{1}H-NMR spectrum of the polyester show the presence of a signal at δ=7-8.5 ppm, which is attributed to aromatic protons in isophtaloyl ring and a number of signals in the δ=2-5 ppm region assigned to -O-CH$_2$-(δ=2.3 and 2.8 ppm), -CH$_2$-Cl (δ=3.55-4 ppm) and  protons (δ=4.5 ppm)

respectively. (Fig. 2)

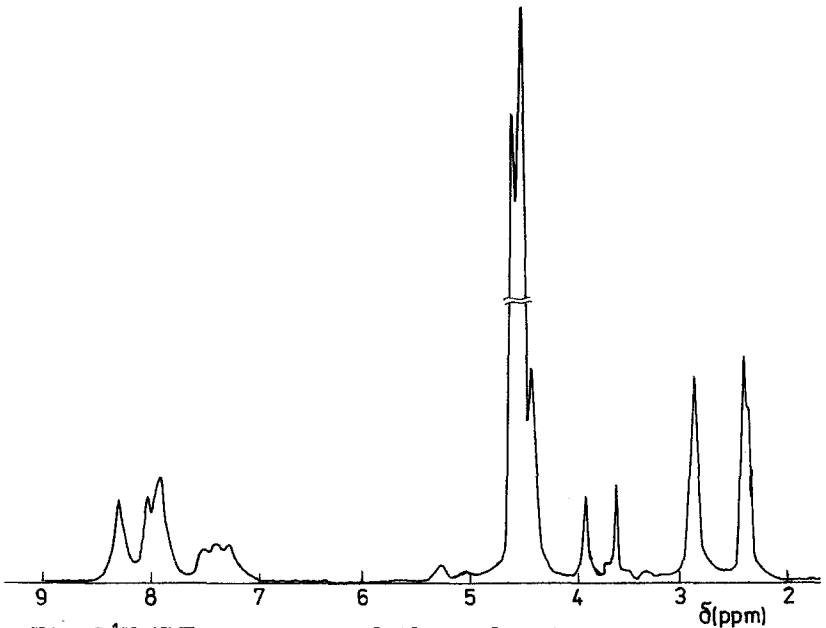


Fig.2 ^{1}H-NMR spectrum of the polyester

Table 1 shows the results obtained with the different catalysts used as phase transfer agents.One should note that polyesterification does not take place without catalyst and that CPyAB is uneffective for this system.It might be that the ion-pair formed between CPyAB and the diisophthalate anion, has a low extraction constant, the catalyst being less efficient in transporting the anion. The best catalytic effect in polyesterification is observed for TEBA.

Table 1. Results of the synthesis of polyesters by the polycondensation of BCMO with potassium isophthalate (solvent DMF; time=4h; T=80°C; catalyst=0.1 mol/l)

PTC	TEBA	TMAC	MTPP	CPyAB	None
Polymer yeld,%	44.3	28.0	22.4	traces	0

Since the reaction occurs in a solid-liquid system one may expect a positive effect of both the temperature and reaction time.This is confirmed by the results presented in Table 2 and Fig.3.

Table 2. Influence of the temperature in polycondensation of BCMO with potassium isophthalate (catalyst:TEBA 0.1 mole/l; solvent:DMF;time=2h)

Temperature °C	60	70	80	90
Polymer yield%	4.4	15.5	23.9	31.5

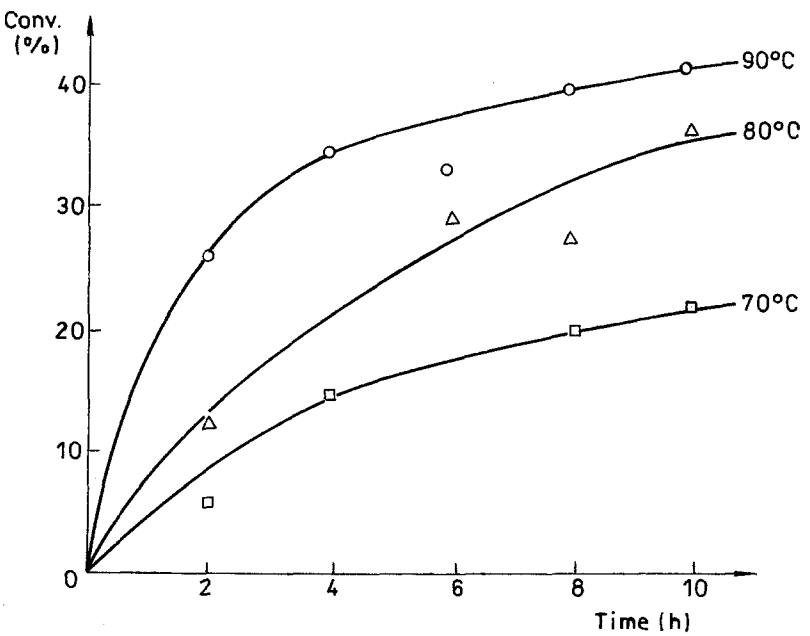


Fig. 3. Conversion vs. time at different temperatures in polycondensation of BCMO with potassium isophthalate.

Derivatographic analysis of the polyesters(samples analysed by DSC also) indicated their considerable high thermal stability with the starting weight loss at about 300°C

DSC analyses (Fig.4) were run for two samples of polyester obtained at 90°C in 2h (a) and 80°C in 8h (b).The first sample reveals the Tg at 34 C and subsequently four thermal transitions located at 43°,125°,170°,and 187°C before isotropization at 206°C.Somewhat different values presents the product obtained at 80°C.Its glass transition occurs at 37°C and is followed also by four thermal transitions, but located at higher temperatures: 61°; 71°; 230°; and 258°C.The isotropization occurs at 284°C.This dissimilarities must account for

differences in the molecular weights of these samples, but the thermal behavior of the polyesters suggests a possible mesomorphism in these samples.It is worth mentioning that these are first heating seans.

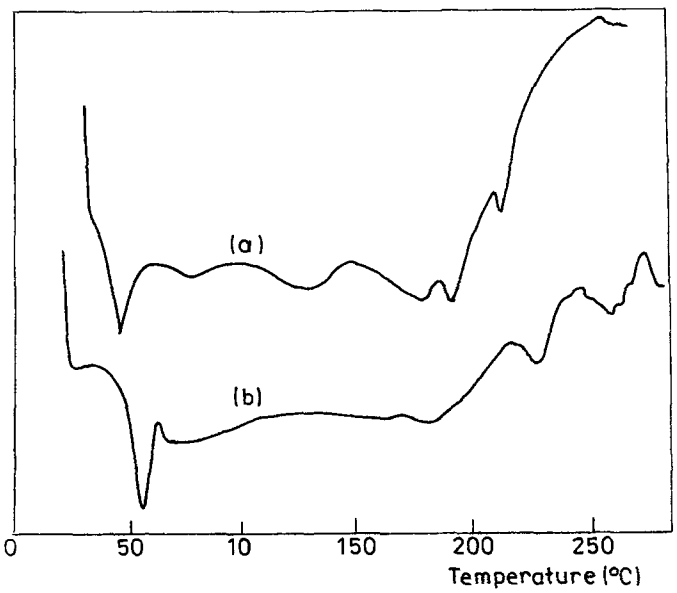


Fig.4 DSC thermograms for samples obtained at 90°C (a) and 80°C (b) (heating rate 10°C/min).

The texture for the first sample at 125°C was depicted by polarizing microscopy sugesting to be a smectic one (Fig.5)

Fig. 5 Optical polarization micrograph of the sample obtained at 90°C,registered at 125°C (x100).

Finally we can conclude that under the PTC conditions it is possible to obtain polyesters from BCMO and metal salts of dicarboxylic acids, but there are few catalysts and organic solvents in which this reaction is successfull.

A possible mesomorphism in such polymers was evidenced.

References

1. Cameron, G.G.Law,K.S.,Mackromol. Chem. Rapid , Commun.,3, 99(1982)
2. Percec,V., Nava,H. ,Jonsson,H.,J. Polym. Sci., Polym. Chem. Ed.,25, 1943(1987)
3. Bulacovschi,V., Simionescu,C.I.,Acta Polym. 36 (4), 191(1985)
4. Tagle,L.H., Diaz,F.R.,Munoz,A.M.,Polym. Bull., 11, 493(1984)
5. Saga,K., Hosoda,H., Ikeda,S., J. Polym. Sci.,Polym Chem. Ed., 17 517(1979)
6. Tagle,L.H., Diaz,F.R., Valdebenito,N., Polym. Bull., 18, 479(1987)
7. Tagle,L.H., Diaz,F.R., De La Maza,M.P., Polym. Bull. 18, 485(1987)
8. Shaffer,T.D., Percec,V., J.Polym.Sci., Polym.Chem.Ed. 24, 451(1986)
9. Shaffer,T.D., Kramer,M.C., Makromol.Chem.,191, 71(1990), Ibidem Makromol.Chem. 191, 3157(1990)
10. Lee Yu-Der, Tsai Hong-Bing, J.Polymer Sci., Polym. Chem. Ed.,26, 2039(1988).
11. Kielkiewicz,J., Kuran,W., Pogorzelska,B.,Makromol. Chem., Rapid Commun., 2, 255(1981).
12. Polish. Patent 122553(1984); Ref.J.Him.,2C433(1985).

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