Polymer Bulletin 18, 479–483 (1987)

Polymer Bulletin

Polymerization by phase transfer catalysis

6. Synthesis and thermal degradation of phenolphthalein polythiocarbonate*

L.H. Tagle, F.R. Díaz, and N. Valdebenito**

Organic Synthesis Laboratory, Faculty of Chemistry, Catholic University of Chile, P.O. Box 6177, Santiago, Chile

Summary

Phenolphthalein polythiocarbonate was obtained by phase transfer catalysis using several catalysts and characterized by inherent viscosity, i.r. spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. From the thermogravimetric curve, the kinetics parameters were determined. Glass transition temperature, thermal decomposition temperature, activation energy, and preexponential factor were lower than those determined for the corresponding polycarbonate.

Introduction

Phenolphthalein polycarbonate and other related polymers have received attention in order to determine its properties and optimal conditions of synthesis. Interphasial and low temperature synthetical methods have been described and the physical, thermal and mechanical properties, and flammability characteristics have been studied (1-4). Lin and col. (3) have carried out a complete study of the thermal degradation of this polycarbonate, concluding that the degradation is very complex, which include random scission rearrangements, hydrolysis, Friedel-Crafts acylation, and cross-linking. By the other hand, the synthesis was developed principally by Morgan (1) by interphasial or low temperature solution polycondensations.

However, phenolphthalein polythiocarbonate has not been systematically studied, and only Morgan refers to this polymer without greater studies (1), and its thermal properties are not described.

Continuing our works on the application of phase transfer catalysis (PTC) technique to polymer synthesis (5), in this work we report the phenolphthalein polythiocarbonate synthesis, its thermal properties, glass transition temperature (Tg) and thermal degradation temperature (TDT), calculated kinetic parameters, activation energy (E) and preexponential factor (A), and finally are compared with those reported for the corresponding polycarbonate.

---

* For part 5, see ref. 5

** To whom offprint requests should be sent

Experimental part

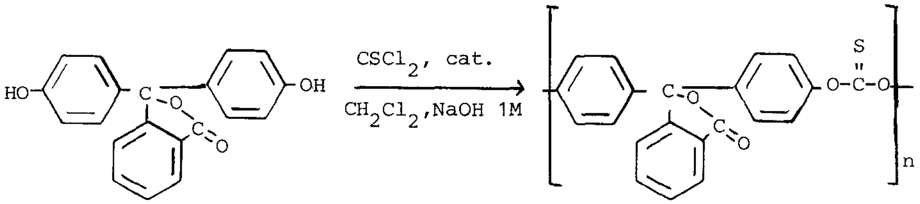
Phenolphthalein, thiophosgene and solvents (Merck) were used without further purification. The following catalysts (Fluka) were used: TBAB, tetrabutylammonium bromide; BTEAC, benzyltriethylammonium chloride; HDTMAB, hexadecyltrimethylammonium bromide; HDTBPB, hexadecyltributhylphosphonium bromide; and Aliquat, methyltrioctylammonium chloride.

The IR spectrum was recorded on a Perkin-Elmer 1310 spectrophotometer. Viscosimetric measurements were made in a Desreux-Bischoff (6) type dilution viscosimeter in $CHCl_3$ at 25°C. The Tg value was obtained in a Perkin-Elmer DSC-1B differential scanning calorimeter at 16°C/min under N_2, and the thermogravimetric analysis in a Perkin-Elmer TGS-1 thermobalance at 20°C/min under N_2.

In a typical polycondensation reaction, 5 mmol of phenolphthalein and 0.5 mmol of the catalyst dissolved in 20 mL of 0.5 M NaOH were mixed with 20 mL of CH_2Cl_2. Then, 5 mmol of thiophosgene dissolved in 15 mL of CH_2Cl_2 were added. The mixture was stirred at 20°C and, at the middle of the time, 2.5 mmol of thiophosgene in 5 mL of CH_2Cl_2 were added. Then, the organic layer was separated and poured into methanol. The precipitated polymer was filtered, washed with methanol and then dried under vacuum at 40°C.

Results and Discussion

Phenolphthalein polythiocarbonate was obtained according the following reaction:



using two equivalents of alkali since three equivalents of alkali inhibit polymerization (1).

The white powered polymer was characterized by it IR spectrum, which shows characteristic absorption bands at 1750 cm^{-1} (C=O of the lactone ring), 1200 cm^{-1} (C=S of the thiocarbonyl group), 830 and 750 cm^{-1} (out-of-plane CH deformation vibrations of p- and o-substituted phenyl respectively).

In absence of catalyst, a value of ηinh= 0.08 dL g^{-1} (in $CHCl_3$ at 25°C and c= 0.5 g/dL) and a yield of 80% were obtained, due probably to a interphasial polycondensation between thiophosgene dissolved in the organic phase and the alkaline phenolphthalein in the aqueous phase.

Table I shows the results obtained with the catalysts used as phase transfer agents. TBAB and HDTBPB were practically uneffective as catalysts for this system and the yields and ηinh obtained can be explained by a intherphasial polycondensation process, probably due to their lypophilic character which make difficult to transport this lypophilic dianion. Something similar occurs with Aliquat, exept at 10 min, and then ηinh decrease due to a probable hydrolitic process, which has been described in other systems (5).

TABLE I. Yields and inherent viscosities obtained for phenolphthalein polythiocarbonate

Time[a] / Catalyst	10 %	10 ηinh[b]	30 %	30 ηinh[b]	150 %	150 ηinh[b]
TBAB	80	0.13	80	0.11	85	0.13
BTEAC	77	0.20	79	0.22	82	0.16
HDTMAB	85	0.22	96	0.19	89	0.18
HDTBPB	71	0.12	87	0.11	85	0.11
Aliquat	87	0.16	88	0.14	86	0.11

a: minutes
b: $dL \cdot g^{-1}$ in $CHCl_3$ at 25°C, c= 0.5 gr/dL

BTEAC and HDTMAB were more effective as catalysts for this system. BTEAC is a hydrophilic catalysts (7) and this make it capable of transferring lypophilic dianions as this. Furthermore this catalyst has Cl^- as counterion, which is exchanged more easily than Br^-. HDTMAB, by structure one long lypophilic chain and three methyl groups, has the characteristics of a micellar agent (8), and a process of this kind is impossible to rule out.

A glass transition temperature (Tg) of 238°C was obtained for this polythiocarbonate, which is lower than the value described (272°C) for the corresponding polycarbonate (2). This behaviour has been described by us for a serie of polythiocarbonates (9), furthermore the rigidity factor σ found by us for those polythiocarbonates from dilute solution viscosity measurements (10,11) showed that this steric hindrance parameter is lower for polythiocarbonates than for polycarbonates. This has been explained in terms of the different contribution to the partial double bond character of the CO-O and CS-O groups (9).

Figure 1 shows the thermogravimetric analysis of this polythiocarbonate, and the thermal decomposition temperature (TDT) was 415°C, which was taken as the first strong change of the slope in the thermogravimetric curve. This value is lower than that described (483°C) for the corresponding polycarbonate (2).

The thermal decomposition kinetic of the thermogravimetric weight loss data were attributed to the kinetic equation 1.

$$\frac{-d\alpha}{dt} = k_n \, (1-\alpha)^n \qquad (1)$$

where α is the sample weight fraction reacted at time t and k_n the specific rate at reaction order n. The reaction rates $d\alpha/dt$ were calculated

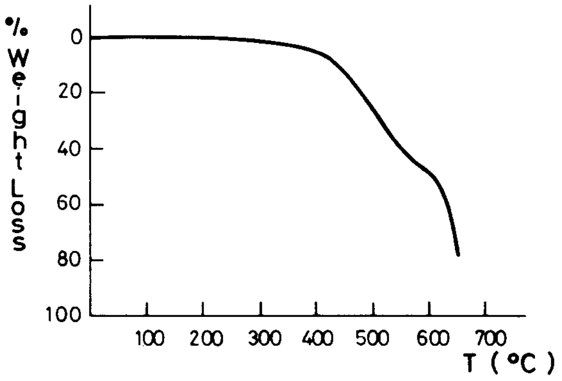


Fig. 1. Thermogravimetric curve of phenolphthalein polythiocarbonate.

using a differential technique and directly incorporating the heating rate (20°C/min) into the data of temperature versus weight fraction (12). The specific rate k_n was obtained from the Arrhenius relation 2.

$$k_n = A\, c^{-E/RT} \qquad (2)$$

where A is the preexponential factor, E the activation energy, T the absolute temperature, and R the gas constant. The expresions 1 and 2 were combined and used it logarithmic form 3.

$$\beta = \ln\left[\frac{-d\alpha/dt}{(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \qquad (3)$$

A linear multiple regression program was developed to calculate the kinetics parameters E and A from a linear least-squares fit of the data in a semilogarithmic plot of β versus 1/T, which is showed in the figure 2. The first-order model was the best fit for the kinetics data for this polythiocarbonate between 410 and 550°C, and we obtained a value of 25.9 kcal/mol as activation energy and $9.31\cdot10^4$ sec^{-1} as preexponential factor, which are lower than those described for the corresponding polycarbonate, 42,6 kcal/mol and $5.15\cdot10^9$ sec^{-1} respectively (3).

This lower E value shows that the thiocarbonyl group exert a great influence in the kinetic of the degradation, and the energy necessary to begin the decomposition is lower. In spite of the first-order reaction suggests a random scission, it is probably that this polythiocarbonate undergo complicated thermal degradation which included random scission, rearrangement, hydrolysis and cross-linking, as has been described for phenolphthalein polycarbonate degradation. The low value of the preexponential factor probably can to confirm the cross-linking between the chains, furthermore the thiocarbonate group and the lactone ring are both suceptible to thermal deterioration (3).

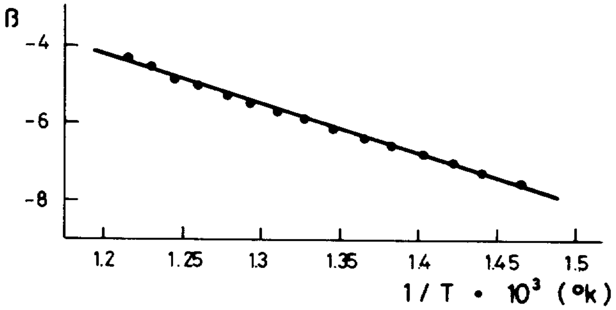


Fig. 2. Arrhenius plot for the degradation of phenolphthalein polythiocarbonate.

Finally we can conclude that phase transfer catalysis is a suitable method for to obtain phenolphthalein polythiocarbonate of moderate molecular weight, being BTEAC an apropiate catalyst. The thermal behaviour of this polythiocarbonate shows that Tg and TDT values and the kinetics parameters are lower than those described in the literature for the corresponding polycarbonate.

Acknowledgements

The authors thank to "Dirección de Investigación (DIUC)" of the "Pontificia Universidad Católica de Chile" for finantial support.

References

1. P.W. Morgan, J. Polym. Sci., Part A, 2, 437 (1964)
2. J.A. Mikroyannidis, Eur. Pol. J., 22, 125 (1986)
3. M.S. Lin, B.J. Bulkin and E.M. Pearce, J. Polym. Sci., Pol. Chem.Ed., 19, 2773 (1981)
4. M.S. Lin and E.M. Pearce, J. Polym. Sci., Pol. Chem. Ed., 19, 2659 (1981)
5. L.H. Tagle and F.R. Diaz, Eur. Pol. J., in press (1987)
6. V. Desreux and F. Bischoff, Bull. Soc. Chim. Belg., 59, 93 (1950)
7. R. Bar, L. Karpug-Bar, Y.Sasson and J. Blum. Anal. Chim. Acta, 154, 203 (1983)
8. C.M. Starks and C. Liotta, "Phase Transfer Catalysis, Principles and Techniques", Academic Press, New York 1978, p. 42
9. M. Yazdani-Pedram, E. Soto, L.H. Tagle, F.R. Diaz, L. Gargallo and D. Radic, Thermochim. Acta, 105, 149 (1986)
10. L. Gargallo, E. Soto, F.R. Diaz, L.H. Tagle and D. Radic, Eur. Pol. J., in press (1987)
11. L. Gargallo, E. Soto, L.H. Tagle and D. Radic, unpublished results
12. W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22, 2285 (1978)

Accepted April 5, 1987 C