Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polycarbonate Resins: Synthesis and Thermogravimetric Analysis

L. H. Tagle[a]; F. R. Diaz[a]
[a] Organic Synthesis Laboratory Faculty of Chemistry, Catholic University of Chile, Santiago, Chile

To cite this Article Tagle, L. H. and Diaz, F. R.(1991) 'Polycarbonate Resins: Synthesis and Thermogravimetric Analysis', Journal of Macromolecular Science, Part A, 28: 3, 397 — 411

To link to this Article: DOI: 10.1080/00222339108052150

URL: http://dx.doi.org/10.1080/00222339108052150

J. MACROMOL. SCI.—CHEM., A28(3 & 4), pp. 397–411 (1991)

POLYCARBONATE RESINS: SYNTHESIS AND THERMOGRAVIMETRIC ANALYSIS

L. H. TAGLE* and F. R. DIAZ

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

ABSTRACT

Resins from diphenols with an aromatic ring as side group, phosgene, and a triphenol as crosslinking agent were synthesized under phase transfer conditions. The resins obtained with a phase transfer catalyst showed higher thermal stability than those obtained without catalyst. The function of the catalyst is to transport triphenol from the aqueous phase to the organic phase. The thermal stability of the resins was related to the structure and the content of triphenol. It was found that resins derived from diphenol I exhibited higher thermal stability as the content of triphenol increased. On the other hand, when diphenol II was used, the thermal stability decreased as the content of triphenol increased, due to steric hindrance of the methyl group on the side ring. Also, a resin from the triphenol alone was synthesized in the same conditions. The kinetic parameters of the decomposition process were determined for all resins.

INTRODUCTION

Dynamic thermogravimetry, defined as a continuous process which involves the measurement of sample weight as the reaction temperature is changed by means of a programmed rate of heating, is a widely used technique for polymer characterization. The applications of thermogravimetry also include comparisons of relative thermal stabilities, the effect of additives on thermal stability, studies of degradation kinetics, and analysis of copolymeric systems [1, 2].

Phase transfer catalysis [3, 4] is a synthetic technique in which the reactant in the aqueous phase interchanges with the anion of the catalyst, normally an onium salt which then transfers in the form of an ion pair to the organic phase; in the latter it quickly reacts with the substrate due to its poor solvation in a low polarity solvent. We have used this technique for the synthesis of several kinds of condensation polymers, such as polyethers [5], polythioethers [6], polythiocarbonates [7–10], polycarbonates [11], and copoly(carbonate–thiocarbonate)s [12], obtaining good yields and high molecular weights. These polymers were characterized and their thermogravimetric behaviors determined [13–16].

The aim of this work is to describe the synthesis of polycarbonate resins from diphenols and phosgene by using a triphenol as the crosslinking agent with and without a phase transfer catalyst to compare the thermal stability of the resins and to determine the kinetics parameters of the decomposition according to the method described by Wen and Lin [17]. We have also determined the influence of the catalyst in the synthetic process, measured by the thermal stability of the resins due to their insolubility.

EXPERIMENTAL

Monomers 1,1-bis(4-hydroxy-phenyl)-1-phenyl-ethane (I) and 1,1-bis(4-hydroxy-phenyl)-1-(4-methyl-phenyl)-ethane (II) were synthesized according to a procedure described previously [11, 18]. 1,1,1-Tris(4-hydroxy-phenyl)-ethane (III) (from Aldrich), benzyltriethylammonium chloride (BTEAC), and phosgene (20% in toluene, from Fluka) were used without further purification.

In a typical polycondensation reaction, 2.5 mmol monomer, 0.05 or 0.25 mmol triphenol (2 and 10%, respectively), and 0.125 mmol BTEAC dissolved in 20 mL of 1 *M* NaOH were mixed with 20 mL CH_2Cl_2. Then 1.2 or 1.4 mL of a toluene solution of phosgene in 5 mL CH_2Cl_2 was added. The mixture was stirred at 20°C for 30 min. The precipitated resin was poured into methanol, filtered, washed with methanol, and then dried under vacuum at 40°C.

TABLE 1. Yields and Temperatures for a 10% Weight Loss of the Resins

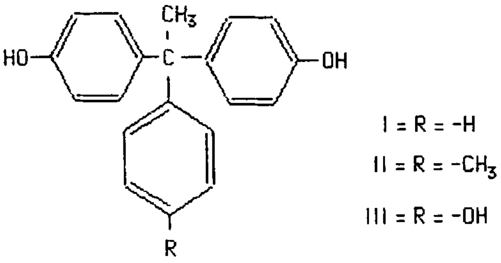
Resin[a]	Yield, %	$T^{10\%}$, °C
I(2)	68	322
I(2)-C	87	382
I(10)	72	445
I(10)-C	76	452
II(2)	49	333
II(2)-C	84	374
II(10)	67	285
II(10)-C	81	330
III	9	270
III-C	8	317

[a] C = resin obtained by using catalyst. Numbers in parentheses are mol% of triphenol.

Dynamic thermogravimetric analyses were carried out in a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (5–7 mg) were placed in the platinum sample holder, and the thermal degradation measurements were carried out between 25 and 650°C at a 20°C min^{-1} heating rate under N_2 atmosphere.

RESULTS AND DISCUSSION

Resins were synthesized from monomers I and II, using 2 or 10% of the triphenol as the crosslinking agent. BTEAC was used as the phase transfer catalyst. A resin using triphenol III alone was also obtained, with and without catalyst. All resins precipitated in the reaction media and were insoluble in common organic solvents. The IR spectra showed a strong band at 1780 cm^{-1}, corresponding to the C=O of the carbonate group. Table 1 shows the yields obtained; 2 and 10 denote the percentage of the crosslinking agent used, and C and BTEAC were used as catalysts.



Without catalyst, the resin was obtained by an interfacial polycondensation process. When BTEAC is used as catalyst, the yields increase due to the more effective transfer of the triphenol. This catalyst was also effective in the synthesis of linear polycarbonates derived from the same monomers [11].

Table 1 also shows the temperature for a 10% weight loss for each resin. Figure 1 shows the thermogravimetric curve for the resins from monomer I. The temperatures at which the resins lose 10% weight increase when the catalyst is used and also when the crosslinking agent content is increased. In both cases the resin will be more highly crosslinked, and as a result they degrade at a higher temperature. However, the number of carbonate groups increases the activity [19–21], which allows for degradation at lower temperatures than the respective linear polycarbonates [14].

Figures 2 and 3 show the thermogravimetric curves obtained for resins derived from monomer II, with and without catalyst, using 2 and 10% of the crosslinking agent (III). The data in Table 1 indicate the temperature for 10% weight loss of the resins. It can be seen that the resins obtained with catalyst show higher thermal stability due to higher crosslinking by triphenol. However, when 10% of the crosslinking agent III is used, thermal stability decreases relative to those resins containing 2% of III. Since the methyl group in the side aromatic ring of II is the only difference, this apparent anomaly may be due to a decrease in charge packing (steric effect), lower molecular weight (solubility effect), or an inherently more reactive methylphenyl.

Resins from triphenol III and phosgene were also prepared. The yields were very low, probably because the product precipitated. Figure 4 shows the thermogravimetric curves of these resins. The resin obtained with BTEAC as catalyst shows a higher thermal stability, indicating that

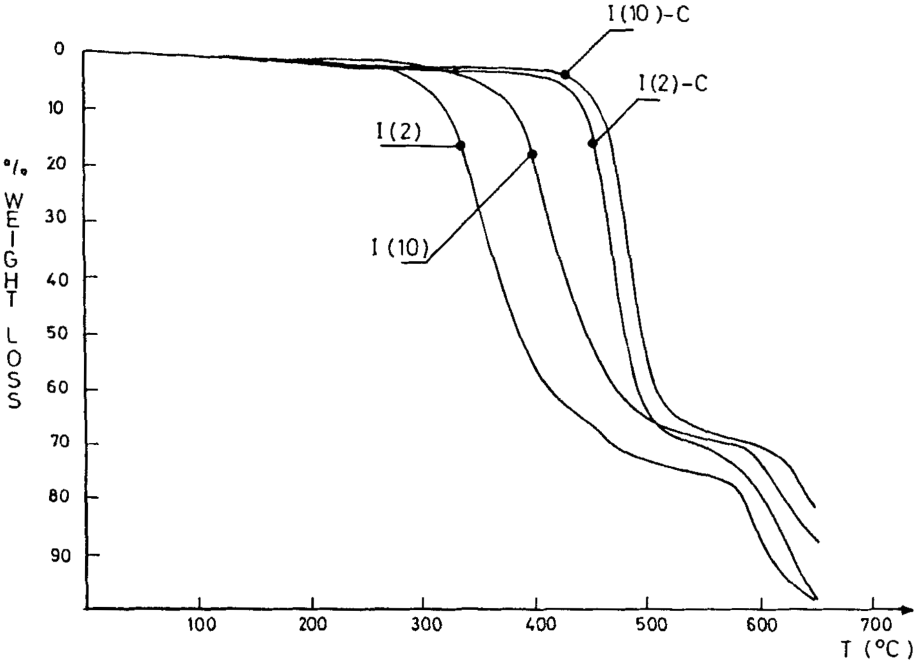


FIG. 1. TG curves for I(2), I(10), I(2)-C, and I(10)-C.

the catalyst is also effective in the synthesis of these types of materials. Without catalyst, the curve shows several stages of degradation which might be due to the degradation of small molecules. However, once more the effectiveness of the catalyst in obtaining more thermally stable resins is illustrated.

The kinetic parameters of thermogravimetric weight loss were calculated by using

$$-(d\alpha/dt) = k_n(1 - \alpha)^n \qquad (1)$$

according to the method developed by Wen and Lin [17], where α is the fraction of the sample weight reacted at time t, and k_n is the specific rate with reaction order n. The reaction rates were calculated by using a differential technique with the heating rate (20°C/min) incorporated

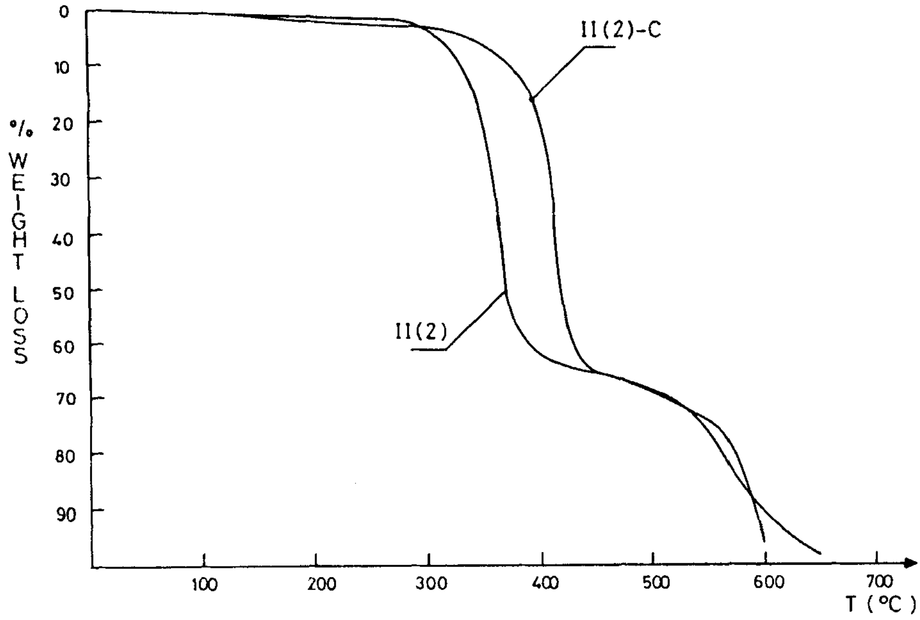


FIG. 2. TG curves for II(2) and II(2)-C.

directly in the data of temperature versus sample weight fraction. The specific rates k_n were obtained from the Arrhenius relation

$$k_n = A \exp(-E/RT) \tag{2}$$

where E is the activation energy, A is the pre-exponential factor, T is the absolute temperature, and R is the gas constant. Equations (1) and (2) were combined and used in logarithmic form:

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

A linear multiple-regression program was developed to calculate the kinetic parameters E and A from a least-squares fit of the data in a semilogarithmic plot of β versus $1/T$ for a given value of n. The linearity of each plot was good, although some scatter was detected at the beginning and end of the decomposition, which can be attributed to the diffi-

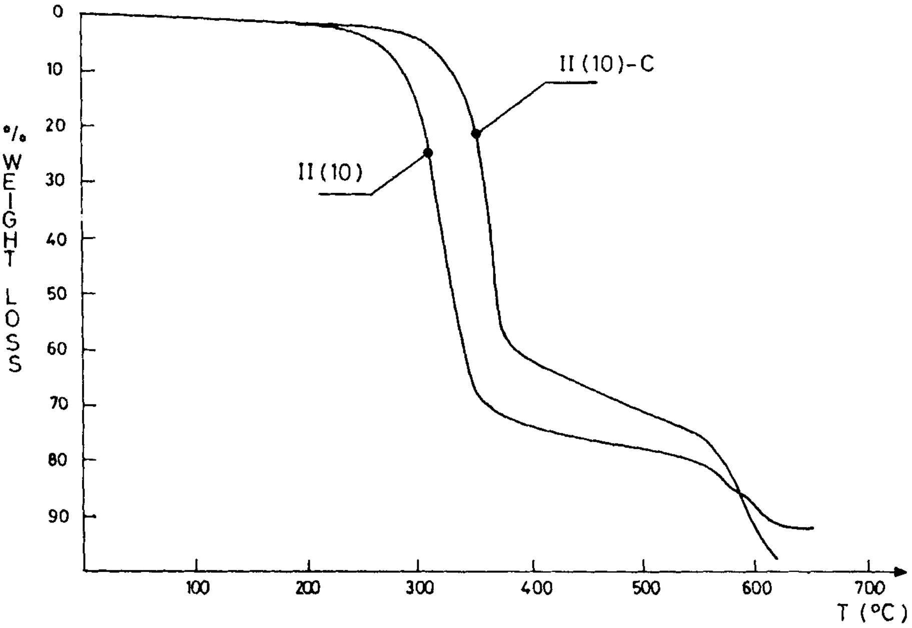


FIG. 3. TG curves for II(10) and II(10)-C.

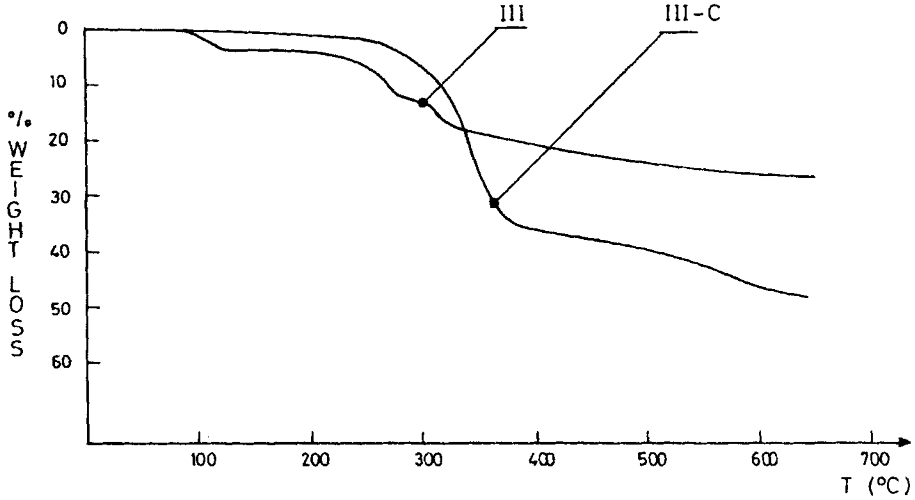


Fig. 4. TG curves for III and III-C.

TABLE 2. Kinetic Parameters of the Resins

Resin[a]	Range, °C	n	E, kcal/mol	A, seg^{-1}
I(2)	280–470	1	25.27	2.12×10^5
	480–560	1	17.35	4.59×10^2
I(2)-C	430–510	1	73.37	1.79×10^{18}
	520–580	1	16.09	7.15×10^1
I(10)	360–490	1	36.91	2.07×10^8
	500–580	1	17.44	3.04×10^2
I(10)-C	440–530	1	71.62	2.12×10^{17}
	530–600	1	20.05	1.02×10^3
II(2)	290–400	0	23.32	2.52×10^4
	410–510	1	8.70	1.68
II(2)-C	320–450	0	19.75	4.63×10^2
	450–550	1	13.00	1.69×10^1
II(10)	260–360	0	18.90	2.27×10^3
	390–540	1	5.26	0.16
II(10)-C	330–390	0	23.64	3.67×10^4
	400–540	1	8.71	1.06
III-C	250–390	0	14.29	3.19×10^1

[a] C = resin obtained by using catalyst. Numbers in parentheses are mol% of triphenol.

culty of obtaining accurate measurements at the extremes of the experiment.

As can be seen from Figs. 1–3, all the resins derived from monomers I and II showed a two-step degradation, which was confirmed by kinetic analysis and can be attributed to a two-step mechanism in the thermal decomposition, as described by several authors [22–24].

Table 2 summarizes the kinetic parameters of the thermal decomposition for all the resins and the temperature range in which each decomposition step occurs. Figures 5–13 show plots of β versus $1/T$ for the resins.

Resins derived from monomer I degrade in two steps, both of which

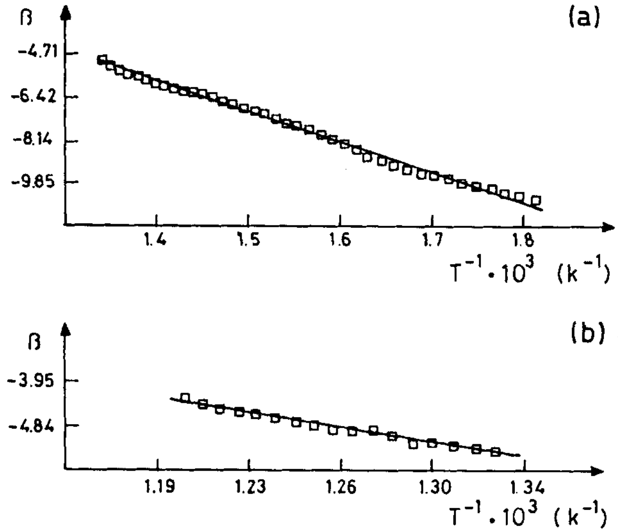


FIG. 5. Arrhenius plot for degradation of I(2): (a) 280-470°C, $n = 1$; (b) 480-560°C, $n = 1$.

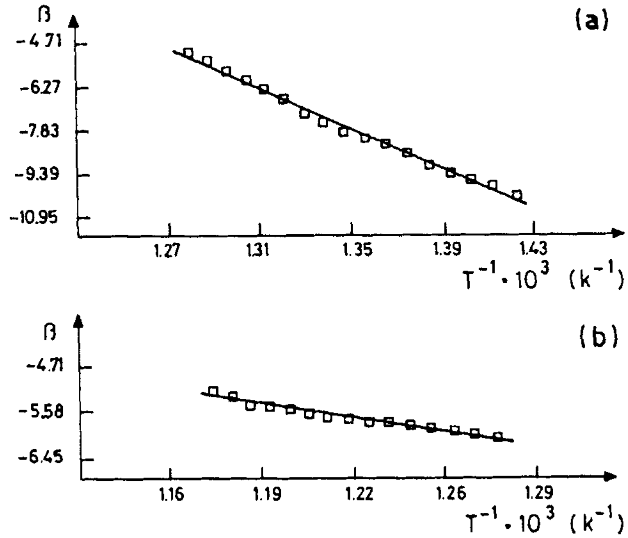


FIG. 6. Arrhenius plot for degradation of I(2)-C: (a) 430-510°C, $n = 1$; (b) 520-580°C, $n = 1$.

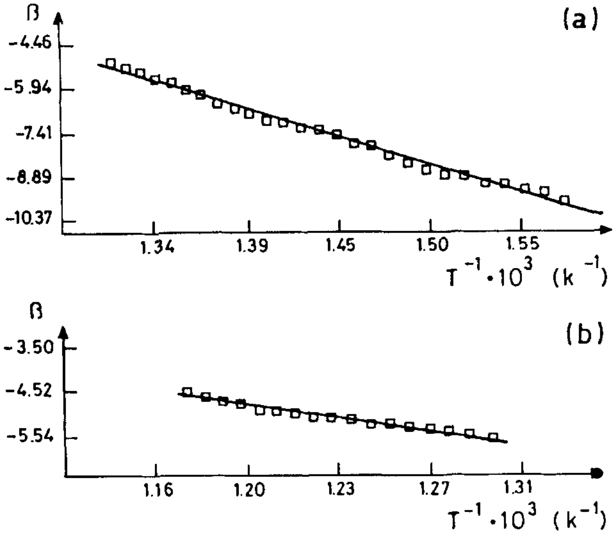


FIG. 7. Arrhenius plot for degradation of I(10): (a) 360–490°C, $n = 1$; (b) 500–580°C, $n = 1$.

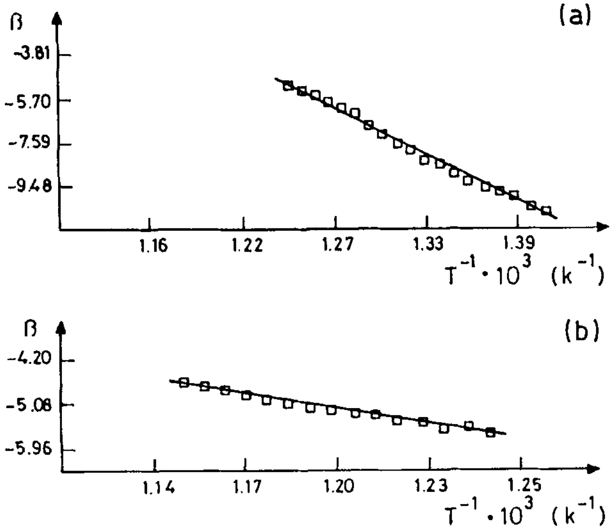


FIG. 8. Arrhenius plot for degradation of I(10)-C: (a) 440–530°C, $n = 1$; (b) 530–600°C, $n = 1$.

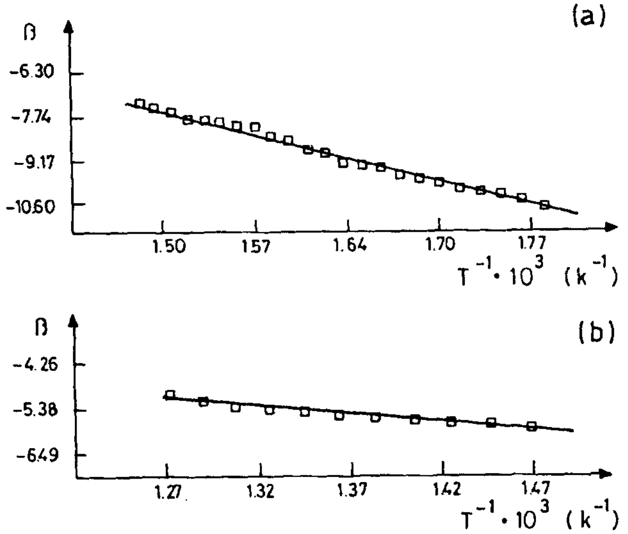


FIG. 9. Arrhenius plot for degradation of II(2): (a) 290–400°C, $n = 0$; (b) 410–510°C, $n = 1$.

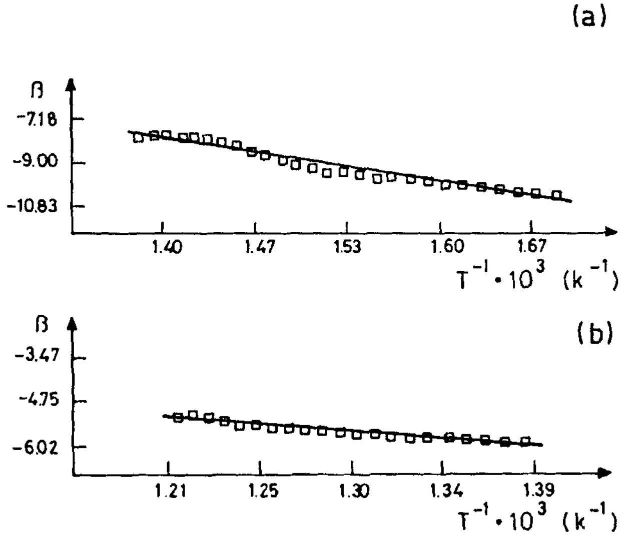


FIG. 10. Arrhenius plot for degradation of II(2)-C: (a) 320–450°C, $n = 0$; (b) 450–550°C, $n = 1$.

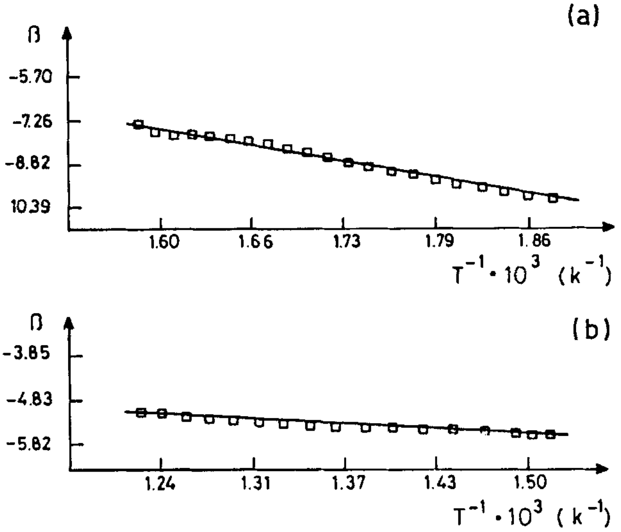


FIG. 11. Arrhenius plot for degradation of II(10): (a) 260–360°C, $n = 0$; (b) 390–540°C, $n = 1$.

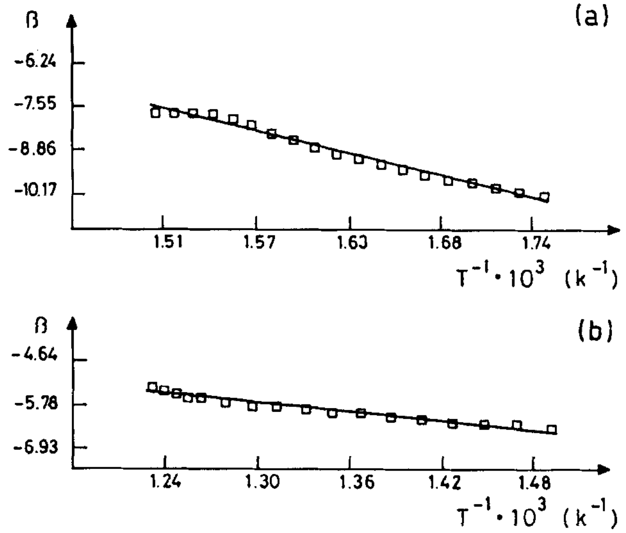


FIG. 12. Arrhenius plot for degradation of II(10)-C: (a) 330–390°C, $n = 0$; (b) 400–540°C, $n = 1$.

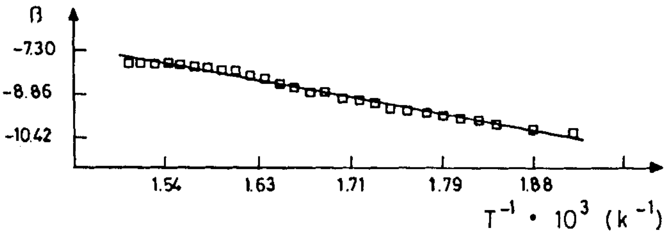


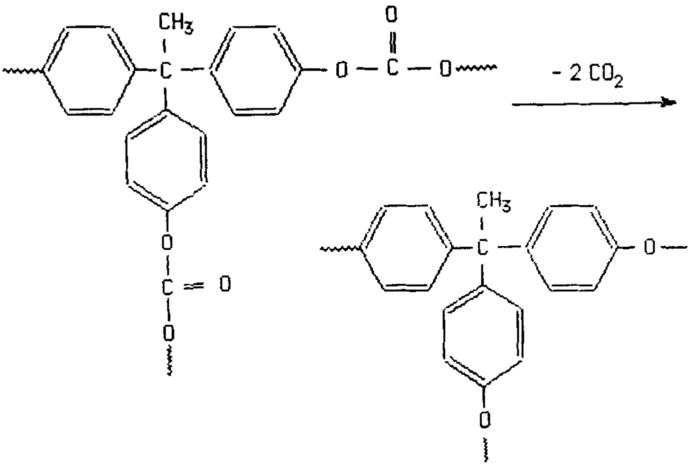
FIG. 13. Arrhenius plot for degradation of III-C: 250–390°C, $n = 0$.

are first order. From the mechanistic point of view, it is probable that the principal reactions can be the decarboxylation of the carbonate group and the rearrangement of this group to form a pendant carboxy group ortho to an ether link in the main chain. The latter may undergo other reactions, especially condensations with other polymeric chains in analogy to the mechanism proposed by Davis and Golden for bisphenol A polycarbonate degradation carried out in a continuously evacuated system [19, 20].

On the other hand, resins derived from monomer II degrade in two steps, the first being zero order and the second first order. It is probable that rearrangement of the carbonate group does not occur with these resins, and the degradation proceeds only by decarboxylation due to the presence of a methyl group in the side ring which prevents new condensation reactions. The thermal stability of these resins is lower than those derived from monomer I which does not have a methyl group in the side ring.

Finally, both types of resins degrade at a lower temperature than the linear polycarbonates which formed insoluble species after a 10% weight loss; this enhanced stability may be due to the formation of crosslinks formed by the reaction of carboxylic groups ortho to an ether linkage in the main chain [11, 19, 20].

The resin prepared only from the crosslinking agent and the catalyst shows a one-step degradation of a zero order due principally to a decarboxylation process. It is probable that there are other reactions in the decomposition process because the residue is higher than 23.5%, which corresponds to the exclusive and complete loss of CO_2 according to the following structure:



For the resin obtained from the crosslinking agent alone, without catalyst, it was not possible to calculate the kinetic parameters due to closely spaced multiple degradations. The weight loss of this resin was 27%, which is close to that which would be obtained from the exclusive loss of CO_2 (23.5%).

In regard to kinetic parameters such as activation energy and pre-exponential factor, it is very difficult to relate them to the decomposition process due to the complexity of degradation reactions. Therefore, assumptions about the kinetic parameters over a particular temperature range may be questionable [25].

CONCLUSIONS

The use of a phase transfer catalyst such as BTEAC is useful for the synthesis of polycarbonate resins when using diphenols and a triphenol as crosslinking agents. The results indicate that when a catalyst is used, an increase in thermal stability is obtained relative to those resins synthesized without catalyst.

ACKNOWLEDGMENT

The authors acknowledge the support of the "Dirección de Investigación" (DIUC) of the "Pontificia Universidad Católica de Chile."

REFERENCES

[1] W. W. Wendlandt, *Thermal Methods of Analysis, Vol. 19, Chemical Analysis*, New York, 1974.

[2] T. Nguyen, E. Zavarin, and E. M. Barral, *J. Macromol. Sci.—Rev. Macromol. Chem., C20*, 1 (1981).

[3] C. M. Starks, *J. Am. Chem. Soc., 93*, 195 (1971).

[4] C. M. Starks and R. M. Owens, *Ibid., 95*, 3613 (1973).

[5] L. H. Tagle, F. R. Diaz, and A. M. Muñoz, *Polym. Bull., 11*, 493 (1984).

[6] L. H. Tagle, F. R. Diaz, M. P. De La Maza, and J. C. Vega, *J. Polym. Sci., Polym. Chem. Ed., 24*, 495 (1986).

[7] L. H. Tagle, F. R. Diaz, J. C. Vega, and P. F. Alquinta, *Makromol. Chem., 186*, 915 (1986).

[8] L. H. Tagle, F. R. Diaz, and P. E. Riveros, *Polym. J., 18*, 501 (1986).

[9] L. H. Tagle, F. R. Diaz, and N. Valdebenito, *Polym. Bull., 18*, 479 (1987).

[10] L. H. Tagle, F. R. Diaz, and M. P. Salas, *J. Macromol. Sci.—Chem., A26*, 1321 (1989).

[11] L. H. Tagle and F. R. Diaz, *Eur. Polym. J., 23*, 109 (1987).

[12] L. H. Tagle, F. R. Diaz, and M. P. Salas, *Ibid., 25*, 549 (1989).

[13] L. H. Tagle, F. R. Diaz, and L. Rivera, *Thermochim. Acta, 118*, 111 (1987).

[14] L. H. Tagle and F. R. Diaz, *Ibid., 144*, 283 (1989).

[15] L. H. Tagle and F. R. Diaz, *Ibid., 154*, 271 (1989).

[16] L. H. Tagle and F. R. Diaz, *Ibid., 160*, 161 (1990).

[17] W. Y. Wen and J. W. Lin, *J. Appl. Polym. Sci., 22*, 2285 (1978).

[18] M. E. McGreal, V. Niederl, and J. B. Niederl, *J. Am. Chem. Soc., 61*, 345 (1939).

[19] A. Davis and J. H. Golden, *Makromol. Chem., 110*, 180 (1968).

[20] A. Davis and J. H. Golden, *J. Chem. Soc., B*, p. 45 (1968).

[21] K. B. Abbas, *Polymer, 21*, 936 (1980).

[22] D. A. Anderson and E. S. Freeman, *J. Polym. Sci., 54*, 253 (1961).

[23] B. V. Kokta, J. L. Valade, and W. N. Martin, *J. Appl. Polym. Sci., 17*, 1 (1973).

[24] Z. Sahraoui, J. C. David, and J. M. Vergnaud, *J. Chim. Phys., 76*, 41 (1979).

[25] I. C. McNeill, *Comprehensive Polymer Science*, Vol. 6 (G. Allen, ed.), Pergamon, London, 1989, p. 456.

Received September 6, 1990