Polymer Bulletin 33, 97–101 (1994)

Polymer Bulletin

Thermal degradation of copolymers based on 2-substituted oxazolines and β-methylhydrogenitaconate

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SUMMARY

The thermal stabilities of poly(β-methylhydrogenitaconate-co-2-methyl-2-oxazoline) and poly(β-methylhydrogenitaconate-co-2-ethyl-2-oxazoline) obtained by spontaneous copolymerization have been studied by programmed thermogravimetric analysis over the temperature range from 293 K to 773 K under a flow of nitrogen. Most of the copolymers do not show weight loss until 473 K and they degrade in one step. The kinetic parameters Ea, n and A were obtained following one method of thermogravimetric analysis. The reaction order for all copolymers was 1.0. The poly(β-methylhydrogenitaconate-co-2-methyl-2-oxazoline)s were the most thermostable copolymers.

INTRODUCTION

In the last years, a wide variety of polymers were synthesized in response to the need of materials that retain useful properties at 400°C or higher. The prevention of fire, improvement of aircraft-survival and development of improved materials for space vehicles are some examples. Thermally stable polymers are usually comprised of hetero-aromatic or aromatic chains which lead to high mechanical strength and modulus (1-8).

By far, dynamic thermogravimetric analysis (TGA) is the most widely used method for comparing the stabilities of high-temperature polymers. TGA data provide information about the treshold temperature at which major fragmentation occurs which is an indication of the inherent stability of the polymer structure. It is particularly useful when applied to a homologous series of polymers. Kinetic parameters such as activation energy Ea, pre-exponential factor A and reaction order n give a quantitative measure of the thermal stability (9).

We have reported previously the thermal behaviour of copolymers obtained by zwitterion copolymerization (10-12).

In this study, samples of poly(β-hydrogenmethylitaconate-co-2-methyl-2-oxazoline) and poly(β-hydrogenmethylitaconate-co-2-ethyl-2-oxazoline) obtained by copolymerization via zwitterion (13,14) were degraded under dynamic conditions. This paper reports the data of the thermal stability of these polymers obtained by TGA. The investigation also involves the variation of the kinetic parameters of the thermal degradation of copolymer samples with copolymer composition.

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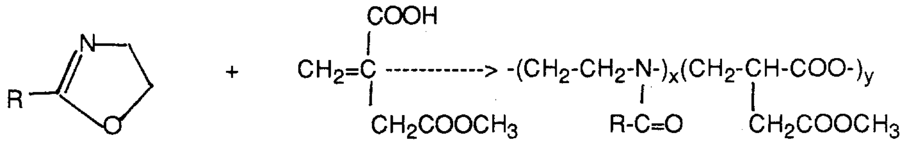
EXPERIMENTAL

Copolymers: All copolymer samples were synthesized at 60°C, for 48 h in CH_3CN by copolymerization via zwitterion without a catalyst (13-14). The copolymer composition was determined by elemental analysis and ^{1}H-NMR spectra.

Thermogravimetric Analysis: The TGA thermograms were obtained using a Perkin Elmer thermobalance TGS-1. Samples of 3-7 mg were degraded under a dynamic nitrogen atmosphere at 10°C min^{-1}.

RESULTS AND DISCUSSION

Homo- and copolymerization reactions usually require the presence of an initiator, catalyst or high radiation energy. However, there have been reports on copolymerization without any added initiator (15-18). Copolymerization of this type is based on a specific interaction of two monomers: one is nucleophilic (MN) and the other is electrophilic (ME). This interaction produces a "genetic zwitterion" $^+MNME^-$ the key intermediate responsible for initiation as well as for propagation. On the basis of the spontaneous copolymerization concept, 2-methyl-2-oxazoline (MOX) and 2-ethyl-2-oxazoline (ETOX) as MNs were copolymerized with β-methylhydrogenitaconate (MHI) as ME.



$$+ \quad CH_2=\underset{CH_2COOCH_3}{\overset{COOH}{\underset{|}{\overset{|}{C}}}} \text{ ------------> } -(CH_2\text{-}CH_2\text{-}\underset{R\text{-}C=O}{\underset{|}{N}}\text{-})_x(CH_2\text{-}\underset{CH_2COOCH_3}{\underset{|}{CH}}\text{-}COO\text{-})_y$$

R = $-CH_3$ (MOX); $-CH_2CH_3$ (ETOX)

In both copolymerization systems the same feed monomer ratio gave a higher incorporation of the electrophilic monomer (ME). When MN is MOX, which exerts less steric hindrance, a copolymer with a higher incorporation of ME was obtained.

The most stable copolymer was sample 3 with a residual weight of 37%. For the poly(β-methylhydrogenitaconate-co-2-methyl-2-oxazoline), sample 6 was the most stable with a residual weight of 26%.

The thermal stability was studied by TGA which has the advantage of being rapid and reproducible under carefully controlled experimental conditions. Stabilities obtained from TGA curves are sensitive to experimental variables, such as particle size and the rate of temperature rise.

Table 1 shows thermal decomposition temperatures (TDTs) for each copolymer. These were taken at the first marked change in the slope of the TG curve.

Table 1. Thermal decomposition temperature and weight-loss at different temperatures of the poly(β-methyl-hydrogenitaconate-co-2-methyl-2-oxazoline), samples 1-3 and poly(β-methylhydrogenitaconate-co-2-ethyl-2-oxazoline), samples 4-6.

Sample	Copol. Composition MN/ME[a)]	$TDT_{10\%}$ (in K)	Weight-loss (%) at different temperatures (in K)				
			373	473	573	673	773
1	1.0 : 1.3	453	7	0	37	57	68
2	1.1 : 1.0	473	0	0	39	61	73
3	1.0 : 1.8	483	0	0	26	55	63
4	1.0 : 1.2	473	0	5	29	57	77
5	1.0 : 1.1	468	0	3	60	74	79
6	1.0 : 1.3	483	0	0	43	71	74

a) Determined from ^{1}H-NMR spectra.

Most copolymers are completely thermostable until 473 K (see Table 1). They are related with Ea values (see Table 2). The copolymers with the greatest Ea have the highest TDT values (see Table 2; copolymers 3 and 6).

The thermal decomposition kinetics of the thermogravimetric weight-loss were studied by using the following equation:

$$-\frac{d\alpha}{dt} = Kn(1-\alpha)^n$$

where Kn is the specific rate, n the reaction order and α the fraction of the sample weight reacted at time t. The reaction rate dα/dt was calculated using a differential technique and including the heating rate v (19). Kn was obtained from the Arrhenius relationship:

$$Kn = A \exp(-Ea/RT)$$

By combining these equations, and using a logarithmic form, the following equation is obtained:

$$\beta = \ln\left[\frac{-v(d\alpha/dT)}{(1-\alpha)^n}\right] = \ln A - \frac{Ea}{RT}$$

By using a linear multiple regression program by plotting β vs 1/T, Ea and A were determined from the slope and intercept (see Figures 1 and 2 and Table 2).

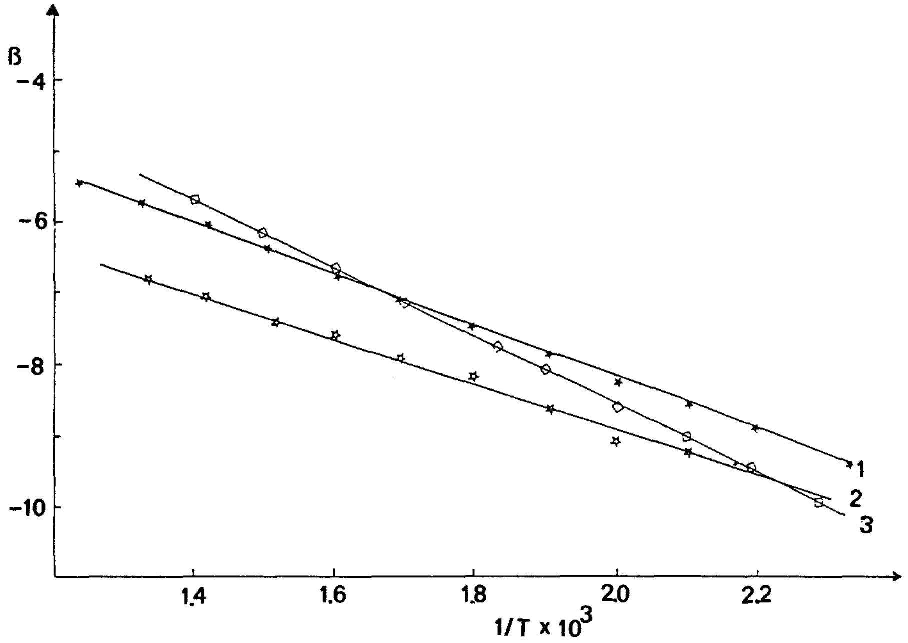


Figure 1. Arrhenius plot for the thermal degradation of copolymers 1-3.

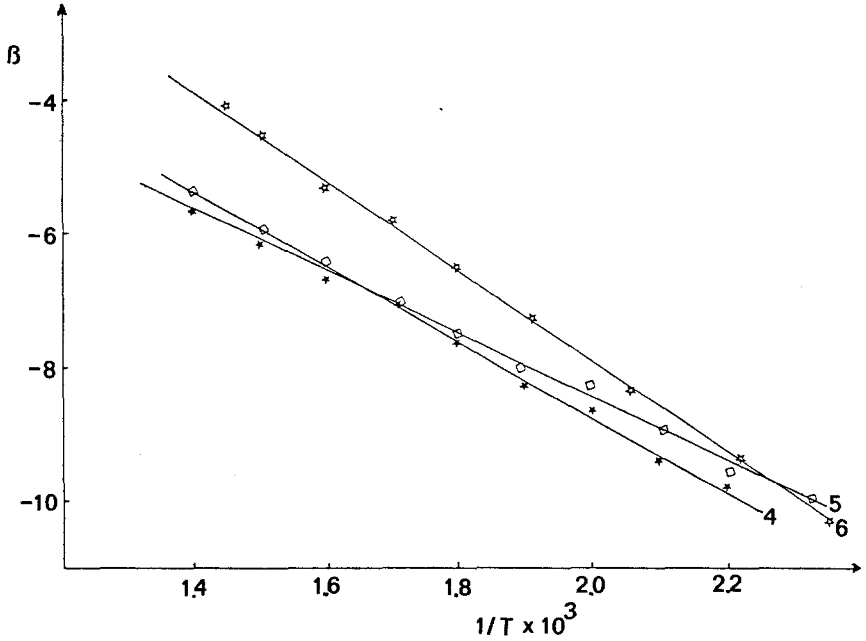


Figure 2. Arrhenius plot for the thermal degradation of copolymers 4-6.

Table 2. Kinetic parameters for the poly(β-methylhydrogenitaconate-co-2-methyl-2-oxazoline)s, samples 1-3 and poly(β-methylhydrogenitaconate-co-2-ethyl-2-oxazoline)s, samples 4-6.

Sample	Copol. Composition[a)]MN/ME	A (s^{-1})	Ea (Kcal/mol)	n	Temperature range (K)
1	1.0 : 1.3	0.394	7.3	1	423-813
2	1.1 : 1.0	0.078	5.3	1	473-653
3	1.0 : 1.8	2.320	9.3	1	423-753
4	1.0 : 1.2	533.300	14.7	1	423-468
4	1.0 : 1.1	18.900	11.7	1	453-723
6	1.0 : 1.3	460.000	17.8	1	463-703

a) Determined from ^{1}H-NMR spectra

As ME increases in the copolymer, the Ea of the degradation increases.

Copolymers 3, and 6 show an Ea = 9.3 Kcal/mol and 17.8 Kcal/mol respectively.

REFERENCES

1. D. Kuman, U. Razdan, A.D. Gupta, *J.* Polym. Sci. Polym. Chem., **31**, 797 (1993).
2. D. Kuman, A. Gupta, M. Khullar, J. Polym. Sci. Polym. Chem., **31**, 707 (1993).
3. P.E. Cassidy, Thermally Stable Polymers, Dekker New York, 1980.
4. Y. Kurachi, I. Okayama, T. Oachasi, J. Polym. Mat. Sci., **24**, 2761 (1989).
5. M. Kayimara, Y. Kurachi, Polymer J., **15**, 104 (1983).
6. H. Kondo, M. Sato, M. Yokoyama, Eur. Polym. J., **16**, 537 (1980).
7. J.M. Barrales-Rienda, J.I. González de la Campa, R.J. González Ramos, J. Macromol. Sci. Chem., **11**, 267 (1977).
8. S. Hoering, S. Jakowlew, J. Ulbricht, Plaste Kautsch., **29**, 622 (1982).
9. A. Rudin, M.C. Samanta, P.M. Reilly, J. Appl. Polym. Sci., **24**, 171 (1979).
10. B.L. Rivas, G. del C. Pizarro, R. Catalán, L.H. Tagle, Thermochim. Acta, **160**, 307 (1990).
11. B.L. Rivas, G. del C. Pizarro, L.H. Tagle, Thermochimica Acta, **184**, 183 (1991).
12. B.L. Rivas, G. del C. Pizarro, R.E. Catalán, L.H. Tagle, Thermochim. Acta, **188**, 163 (1991).
13. B.L. Rivas, G. del C. Pizarro, Polym. Bull., **30**, 515 (1993).
14. B.L. Rivas, G. del C. Pizarro, G. Canessa, Eur. Polym. J., **28**, 1445 (1992).
15. T. Saegusa, Chemtech., **5**, 295 (1975).
16. G. Odian, P.A. Gunatillake, Makromolecules, **17**, 297 (1986).
17. B.L. Rivas, G.S. Canessa, S.A. Pooley, Makromol. Chem., **187**, 71 (1986).
18. B.L. Rivas, G.S. Canessa, S.A. Pooley, Makromol. Chem., **188**, 149 (1987).
19. W.Y. Wen, J.W. Lin, J. Appl. Polym. Sci., **22**, 228 (1978).

Accepted April 6, 1994 K