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

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To cite this Article Negulescu, Ioan I. , Calugaru, Elena-Maria , Vasile, Cornelia and Dumitrescu, Gheorghe(1987) 'Thermal Behavior of Poly(Cr-Cyanoacrylate)S', Journal of Macromolecular Science, Part A, 24: 1, 75 — 83
To link to this Article: DOI: 10.1080/00222338708058510
URL: http://dx.doi.org/10.1080/00222338708058510

J. MACROMOL. SCI.–CHEM., A24(1), pp. 75-83 (1987)

THERMAL BEHAVIOR OF POLY(α-CYANOACRYLATE)S

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ABSTRACT

The thermal degradation of saturated and unsaturated poly(α-cyanoacrylate)s, i.e., poly(methyl α-cyanoacrylate) (PMCA), poly(ethyl α-cyanoacrylate) (PECA), poly(*n*-propyl α-cyanoacrylate) (PPCA), and poly(allyl α-cyanoacrylate) (PACA) has been investigated both in air and nitrogen. The thermal stability of poly(alkyl α-cyanoacrylate)s decreases in the order PPCA > PECA > PMCA. Initially, the thermal stability of PACA is lower than that of PPCA, but at temperatures higher than 220°C the order is reversed due to crosslinking through pendant allylic bonds, which takes place up to 175°C.

INTRODUCTION

The α-cyanoacrylic esters are among the most reactive monomers known, and their anionic polymerization can be initiated by weak covalent bases, even as weak as HO^- from water. Oxygen, CO_2, and H_2O have virtually no effect on the development of polymerization due to the relatively high stability of cyanoacrylate carbanions [1]. Consequently, the monomers together with a plasticizer, a thickener, and a stabilizer (usually SO_2) are used directly as one-component adhesives. The lower members of the series are used for industrial purposes, while the higher homologs (butyl, or even hexyl and heptyl), being wetted well by blood, are used in surgery, e.g., as tissue binders [2, 3].

The main drawback for the application of these materials in electronic or machinery assemblage is the low thermal resistance (80°C) of the adhesive bond. One way to improve the heat resistance of these bonds is to introduce unsaturated cyanoacrylic monomers in the uncured composition [4, 5], with the hypothesis that, following anionic polymerization (curing), the polymer would be able to undergo thermally initiated crosslinking, yielding a three-dimensional adhesive network [6, 7].

In the present paper the thermal behavior of polymers of lower alkyl α-cyanoacrylates (PMCA, PECA, and PPCA) is compared with that of an unsaturated cyanoacrylic polymer (PACA).

EXPERIMENTAL

Methyl, ethyl, *n*-propyl, and allyl α-cyanoacrylates were obtained by a three-step synthesis, i.e., esterification of cyanoacetic acid with the respective alcohol, Knoevenagel condensation of the cyanoacetic ester with CH_2O, and depolymerization of the obtained product to monomeric α-cyanoacrylate in the presence of SO_2 to prevent anionic polymerization [8]. All the polymers were obtained by anionic polymerization of the respective monomers [9].

The thermal behavior of powdered samples was followed both in air and nitrogen using a Mettler TA-1 thermobalance with a heating rate of 10°C/min and a flow rate of gas of 7 L/min. Freshly calcined α-Al_2O_3 was used as the reference for DTA measurements. The activation energies of thermal degradation, $E_{CR}{}^a$ and $E^a_{LR,\alpha=0}$, were determined according to Coats and Redfern [10] and Reich and Levi [11], respectively. $E_{CR}{}^a$ represents the activation energy of the entire process and $E^a_{LR,\alpha=0}$ is the activation energy of thermal decomposition extrapolated to $\alpha = 0$, where α represents the degree of thermal conversion, $\alpha = w_t/w_\infty$ (where w_t is the weight loss at the time t and w_∞ is the weight loss at the end of the decomposition process).

RESULTS AND DISCUSSION

The shape of the DTG and DTA curves of alkyl and alkenyl α-cyanoacrylate polymers (Figs. 1 and 2) gives a first indication of the different thermal behavior of these polyesters. Both DTG and DTA curves of poly(alkyl α-cyanoacrylate)s are simple and composed of only one sharp peak, as exemplified by the thermogram of PECA (Fig. 1), while the thermal decomposition of the unsaturated PACA takes place in three different stages (Fig. 2). However, small dif-

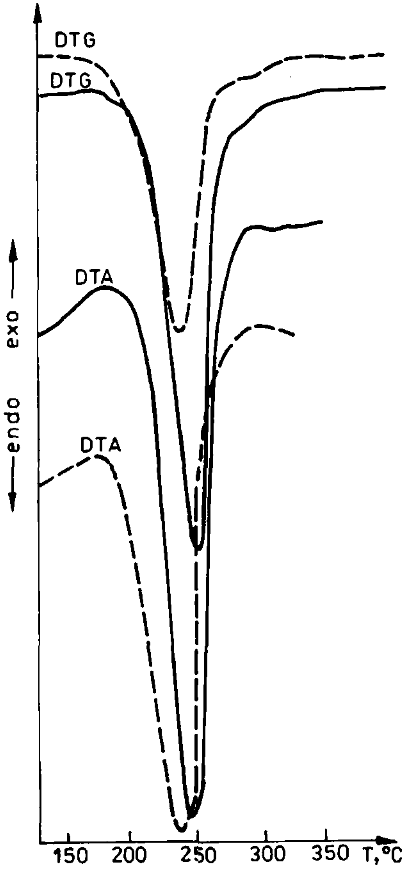

FIG. 1. Thermal degradation of poly(ethyl α-cyanoacrylate) in air (- -) and nitrogen (——).

ferences were noticed for the same polymer depending on whether the sample was heated in nitrogen (Table 1) or in air (Table 2).

Irrespective of the decomposition atmosphere, all saturated poly(α-cyanoacrylate)s are degraded practically completely above 250°C. The temperature range in which the decomposition rate is maximum, ΔT, narrows as the alkyl radical becomes longer if the polymer decomposes in nitrogen but becomes slightly wider in air. These results are as expected if one takes into consideration that, in an inert atmosphere, the degradation occurs through an "unzip-

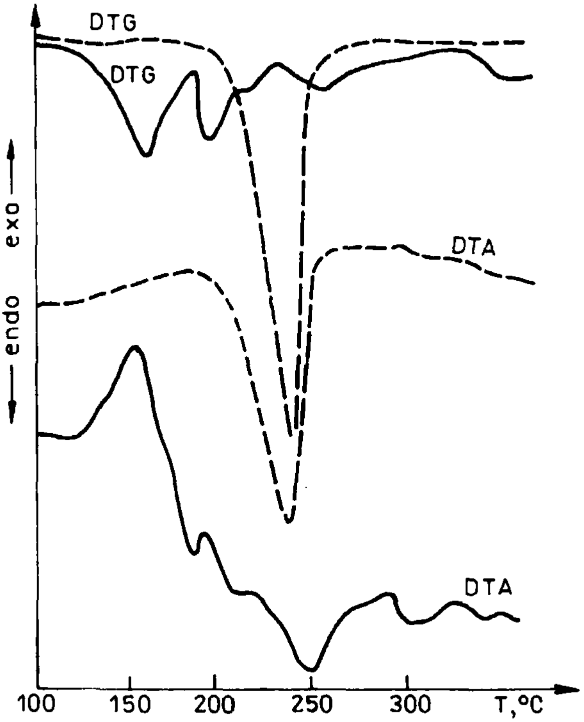

FIG. 2. Thermal degradation in air of poly(*n*-propyl α-cyanoacrylate) (- -) and poly(allyl α-cyanoacrylate) (——).

ping" mechanism, while in air depolymerization is disturbed by certain oxidation reactions.

Tables 1 and 2 show that both $E_{CR}{}^a$ and $E^a_{LR,\alpha=0}$ are lower when the degradation atmosphere is oxidative (air). At the same time, the temperature at which the first weight loss was recorded, T_i, is higher by ~15°C in nitrogen than in air. The increase of T_i from PMCA to PPCA does not necessarily represent increased stability since it may be correlated with the vaporization of the monomer resulting from the "unzipping," i.e., even if the polymers start to decompose (depolymerize to liquid monomer) at the same temperature, the weight loss depends on the volatility of the respective monomer, which decreases with the number of carbon atoms from the alkyl radical. For example, Table 1 indicates that the temperature at which the degradation rate is at its maximum, T_m, is practically the same for thermal decomposition of

TABLE 1. Characteristic Values for Thermal Degradation in Nitrogen of Polymers of Cyanoacrylic Esters

	Decomposition temperature, °C							
Polymer	$T_{i,\mathrm{DTG}}$	$T_{m,\mathrm{DTG}}$	$T_{f,\mathrm{DTG}}$	ΔT^a	$T_{m,\mathrm{DTA}}$	ΔW,[b] %	$E_{\mathrm{CR}}{}^a$, kJ/mol	$E^a_{\mathrm{LR},\alpha=0}$, kJ/mol
PMCA	160	239	278	79	231	93.4	52.3	115.5
PECA	168	244	273	76	236	96.7	73.1	147.0
PPCA	176	244	279	69	233	95.9	79.7	163.8
PACA	127	223	-	96	212	66.0	56.6	109.3
		275	-	148	287	21.4	120.0	198.4
		305	383	178		12.6		

[a] $\Delta T = T_{m,\mathrm{DTG}} - T_{i,\mathrm{DTG}}$.

[b] ΔW = weight loss at $T_{f,\mathrm{DTG}}$.

TABLE 2. Characteristic Values for Thermal Degradation in Air of Polymers of Cyanoacrylic Esters

	Decomposition temperature, °C							
Polymer	$T_{i,\mathrm{DTG}}$	$T_{m,\mathrm{DTG}}$	$T_{f,\mathrm{DTG}}$	ΔT^{a}	$T_{m,\mathrm{DTA}}$	ΔW,[b] %	$E_{\mathrm{CR}}{}^{a}$, kJ/mol	$E^{a}_{\mathrm{LR},\alpha=0}$, kJ/mol
PMCA	148	233	283	75	225	98.3	36.2	73.5
PECA	153	238	324	85	234	93.9	50.8	123.9
PPCA	158	245	291	87	257	97.6	64.1	130.6
PACA	115	158	192	43	153	44.3	39.9	153; 60.4
	192	215	230	23	196	26.3	231.0	300
	230	257	325	27	252	29.5	156.2	220

[a] $\Delta T = T_{m,\mathrm{DTG}} - T_{i,\mathrm{DTG}}$.

[b] ΔW = weight loss at $T_{f,\mathrm{DTG}}$.

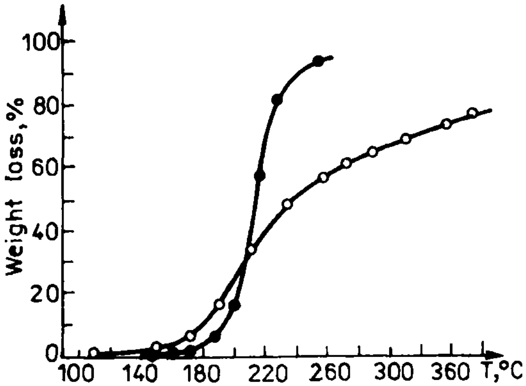

FIG. 3. Thermogravimetric curves for thermal degradation in nitrogen of poly(*n*-propyl α-cyanoacrylate) (●) and poly(allyl α-cyanoacrylate) (○).

PECA and PPCA. At the same time, $T_{m,\mathrm{DTA}}$ (T_m determined from the DTA curve) is lower by ~ 10°C than the corresponding temperature determined from DTG curve, $T_{m,\mathrm{DTG}}$. $E^a_{\mathrm{LR},\alpha=0}$ has similar values for decomposition of PECA and PPCA but is much lower for thermal degradation of PMCA, irrespective of the atmosphere (Tables 1 and 2). However, the total activation energy, $E_{\mathrm{CR}}{}^a$, rises in the order PMCA < PECA < PPCA, both in air and in nitrogen, indicating slightly increased thermal stability for higher homologs. Nevertheless, the final temperature of degradation, $T_{f,\mathrm{DTG}}$, i.e., the temperature at which the last weight loss was recorded, does not differentiate these three polymers (except the degradation of PECA in air, when an anomalous high $T_{f,\mathrm{DTG}}$ was found).

As shown above, the thermal behavior of PACA differs from that of saturated α-cyanoacrylic polymers. If the thermal stability of this unsaturated polyester is compared with that of the saturated homolog, PPCA (Tables 1 and 2), one can see that initially PACA is less stable (T_i and $E_{\mathrm{CR}}{}^a$ are lower) but, since its rate of decomposition is slow, the situation is quite the opposite at higher temperatures (200°C) (Fig. 3). This inversion in the thermal behavior of PACA may be explained by the formation of crosslinks between allylic groups [6], evidenced as an exothermic process in the DTA curve of this polymer between 100 and 175°C (Fig. 2) which makes the degradation of chains by an "unzipping" mechanism more difficult.

The variation of $E_{\mathrm{LR}}{}^a$ with thermal conversion is nonlinear in the case of

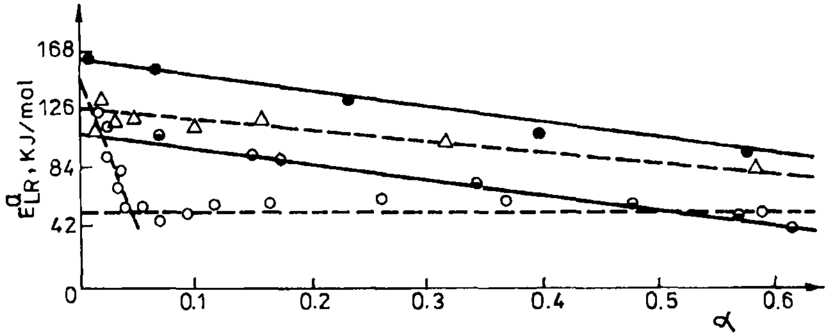

FIG. 4. The dependence of the activation energy, E_{LR}^a, on the thermal conversion, α, for thermal degradation of poly(*n*-propyl α-cyanoacrylate) (Δ, ●) and poly(allyl α-cyanoacrylate) (○, ⊖) in air (--) and nitrogen (—).

thermal degradation of PACA in air (Fig. 4). Two distinct decomposition steps, characterized by different activation energies, can be noted for the same temperature range (140-250°C): one for which $\alpha \leqslant 0.05$ with $E^a_{LR,\alpha=0} = 153$ kJ/mol, and the second, for $\alpha > 0.05$, with $E^a_{LR,\alpha=0} = 60.4$ kJ/mol. For high conversion the activation energy for thermal decomposition of PACA is even lower, ~50 kJ/mol, irrespective of the atmosphere. The next two steps of degradation of PACA are characterized by high values of $E^a_{LR,\alpha=0}$, indicating the formation of rather stable structures (Table 2). An indication for these structures is the carbonaceous material formed during the thermal treatment of PACA while saturated poly(α-cyanoacrylate)s decompose completely.

CONCLUSIONS

The thermal stability of poly(alkyl α-cyanoacrylate)s decreases in the order PPCA > PECA > PMCA. Initially, the thermal stability of PACA is lower than that of PPCA, but for temperatures above 220°C, the order is reversed due to crosslinking through pendant free double bonds which takes place up to 175°C.

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Received December 6, 1985