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 Pathak, Chandrashekhar P. , Patni, Mahendra J. and Babu, Gaddam N.(1987) 'Synthesis, Thermal Properties, and Radiolysis of Poly(Cyclohexyl α-Chloroacrylate)', Journal of Macromolecular Science, Part A, 24: 5, 557 — 566

To link to this Article: DOI: 10.1080/00222338708068141

URL: http://dx.doi.org/10.1080/00222338708068141

J. MACROMOL. SCI.–CHEM., A24(5), pp. 557-566 (1987)

SYNTHESIS, THERMAL PROPERTIES, AND RADIOLYSIS OF POLY(CYCLOHEXYL α-CHLOROACRYLATE)

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ABSTRACT

Cyclohexyl α-chloroacrylate (CCA) was polymerized by radical anionic and γ-radiation initiation. The anionic polymerization of cyclohexyl α-chloroacrylate gave moderately isotactic polymer in toluene and syndiotactic-rich polymer in THF. Poly(cyclohexyl α-chloroacrylate) (PCCA) was found to undergo two-stage weight loss in thermogravimetric analysis, and the first-stage weight loss was attributed to the lactonization reaction. PCCA degraded under γ-radiation, and the radiation yields of crosslinking and scission, G_x and G_s, were 0.6 and 3.8, respectively.

INTRODUCTION

In semiconductor technology, a major effort to produce microcomputer circuits with large memories has been undertaken by many workers [1-3]. This has increased the demand for the development of circuits with submicrometer dimensions. Electron-beam and x-ray lithography offer higher resolution than the conventional UV method. Such fabrication requires resists which are

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sensitive to an electron beam or x-rays. Although poly(methyl α-chloroacrylate) and its copolymers have been studied extensively for this application [2, 3], the other poly(alkyl α-chloroacrylate)s have not been studied.

In the present work we report the synthesis of poly(cyclohexyl α-chloroacrylate) (PCCA) under different experimental conditions and evaluation of the tacticity by IR and 100 MHz NMR spectroscopy. The thermal properties and radiolysis of PCCA are also reported.

EXPERIMENTAL

Polymer Preparation

Cyclohexyl α-chloroacrylate (CCA) was prepared from methyl acrylate according to the literature method [4]. The free-radical polymerizations were carried out by using azobisisobutyronitrile (AIBN) as initiator at 55°C. *n*-Butyllithium was used as anionic initiator for anionic polymerizations at -84°C. The radiation polymerization was initiated with a Cobalt-60 Gamma Chamber-900 supplied by Bhabha Atomic Research Centre, Trombay, at a dose rate of 0.10 ± 0.02 Mrd/h. The polymers were purified by repeated dissolution and precipitation with chloroform-methanol.

Polymer Irradiation

PCCA synthesized by free-radical initiation was used for γ-irradiation and subsequent EPR and molecular weight analysis. Samples were sealed in 5 mm o.d. Pyrex tubes at pressures below 10^{-4} torr and irradiated at 25°C.

Characterization

Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer and the NMR spectra on a Varian XL-100 (100 MHz) instrument. Molecular weight studies were conducted with a Waters gel-permeation chromatograph using THF as the solvent and the universal calibration method. The glass transition temperature (T_g) was determined with a Perkin-Elmer differential scanning calorimeter. A Du Pont-900 thermobalance was used for thermogravimetric analysis (TGA) under nitrogen at a heating rate of 15°C/min. A Varian E-9 X-band instrument was used to record electron spin resonance (ESR) spectra. The radical yield, G_r, was obtained by double integration with a Nicolet microcomputer of the ESR signal with a standard solution of 2,2,6,6-tetramethylpiperidinoxyl as reference.

RESULTS AND DISCUSSION

Table 1 lists the polymerization conditions and polymeric products obtained by the application of radical, radiation, and anionic polymerizations. Typical IR and NMR spectra of PCCA synthesized under these conditions are shown in Figs. 1 and 2. PCCA exhibited two carbonyl absorption peaks, at 1 742 and 1 770 cm^{-1}, and no trace of a C=C stretching peak was detected. The double carbonyl absorption of α-haloesters is indicative of rotational isomerism [5, 6].

The polymers synthesized by free-radical and radiation initiation were about 50-60% syndiotactic. PCCA synthesized by using *n*-butyllithium in THF is of similar syndiotacticity, but PCCA synthesized by using *n*-butyllithium in toluene is moderately isotactic. The proton NMR spectra of these polymers were very similar to each other for the corresponding signals except for backbone methylene protons signals. The backbone methylene protons of the moderately isotactic polymer gave a broad AB quartet, while those of the syndiotactic polymer showed a broad singlet at 2.75 ppm. The effect of the solvent polarity in anionic polymerization on the tacticity of PCCA must be due to ion pair formation, as observed for alkyl methacrylates [7].

The T_g of PCCA is 114°C, which is much higher than for the corresponding poly(cyclohexyl methacrylate), 54°C [8]. Though the methyl group and the chlorine atom at the α-position are of similar size, the higher polarity of the latter may cause higher interchain interactions and, hence, the higher glass-transition temperature.

Thermogravimetric analysis of PCCA showed a two-stage weight loss. The first stage was accounted for by the lactonization reaction, which is a characteristic reaction of poly(alkyl α-chloroacrylate) polymers [9]. The lactone formation was confirmed by observing the lactone absorption frequency at 1 795 cm^{-1} in the IR spectrum of the thermally aged sample (200°C for 2 h).

Table 2 gives the change in number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) after irradiation with various doses. The values of $G_s - G_x$ and $G_s - 4G_x$ were then obtained from the equations [2]:

$$M_n{}^{-1} = \bar{M}_n^{\circ}{}^{-1} + [G_s - G_x]D/100N_A \quad (1)$$

$$\bar{M}_w{}^{-1} = \bar{M}_w^{\circ}{}^{-1} + [G_s - 4G_x]D/200N_A, \quad (2)$$

where G_s and G_x are the radiation yields of crosslinking and scission per 100 eV absorbed, respectively, D is the radiation dose (Mrd), and N_A is Avogadro's number. The G_x and G_s values were obtained by plotting the reciprocal

TABLE 1. Reaction Conditions for the Synthesis of Poly(Cyclohexyl α-Chloroacrylate)

Sample code	Initiator (I)	% I	Solvent	Temperature, °C	Time, h	Yield, %	Tacticity
C_1	AIBN	0.1	–	55	5	28	50-60% syndiotactic
C_2	AIBN	0.1	Toluene	55	7	15	54 + 4% syndiotactic[a]
C_3	AIBN	0.1	THF	55	7	9	50-60% syndiotactic
C_4	γ-Rays	–	–	30	2	12	50-60% syndiotactic
C_5	*n*-Butyllithium	1	THF	-84	3	4	50-60% syndiotactic
C_6	*n*-Butyllithium	1	Toluene	-84	3	3	Moderately isotactic

[a] On triad basis.

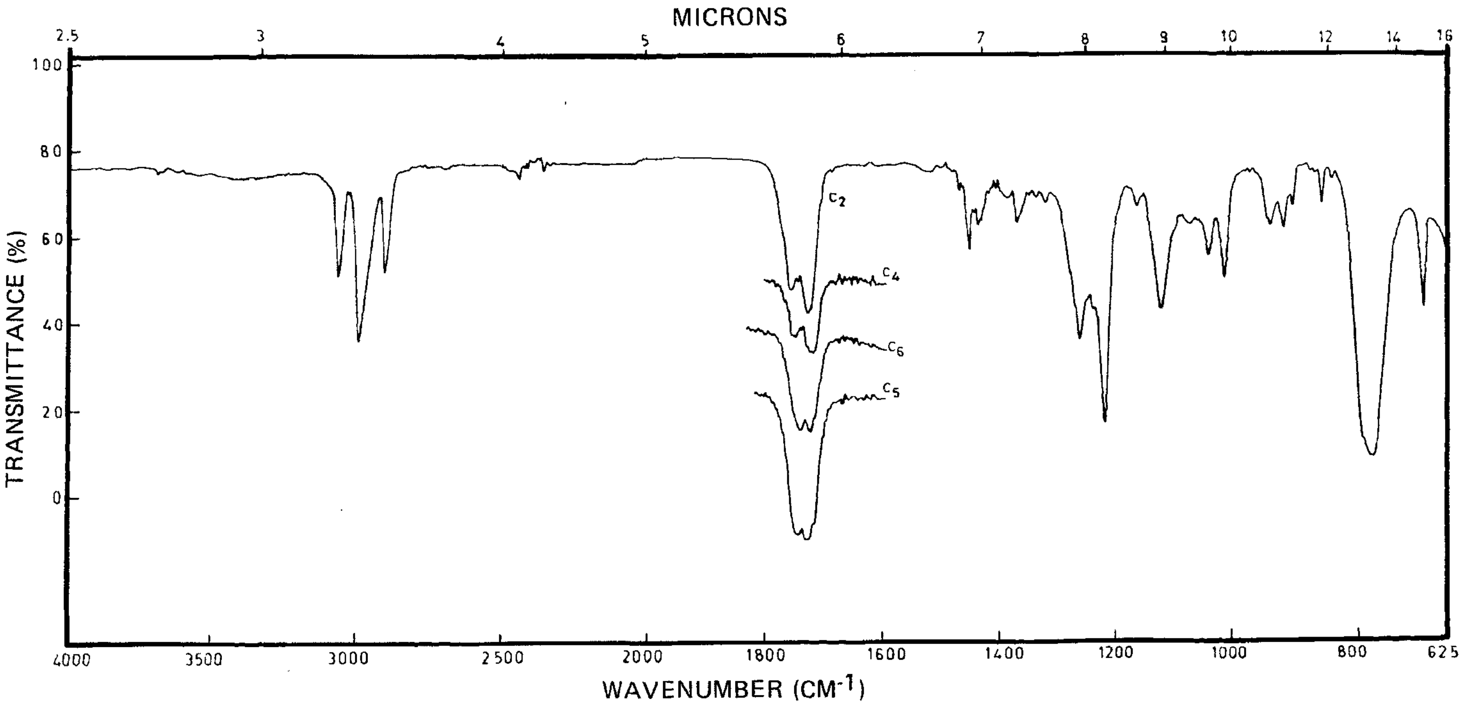


FIG. 1. IR spectra of poly(cyclohexyl α-chloroacrylate)s synthesized under various conditions (see Table 1). Spectra measured in $CHCl_3$.

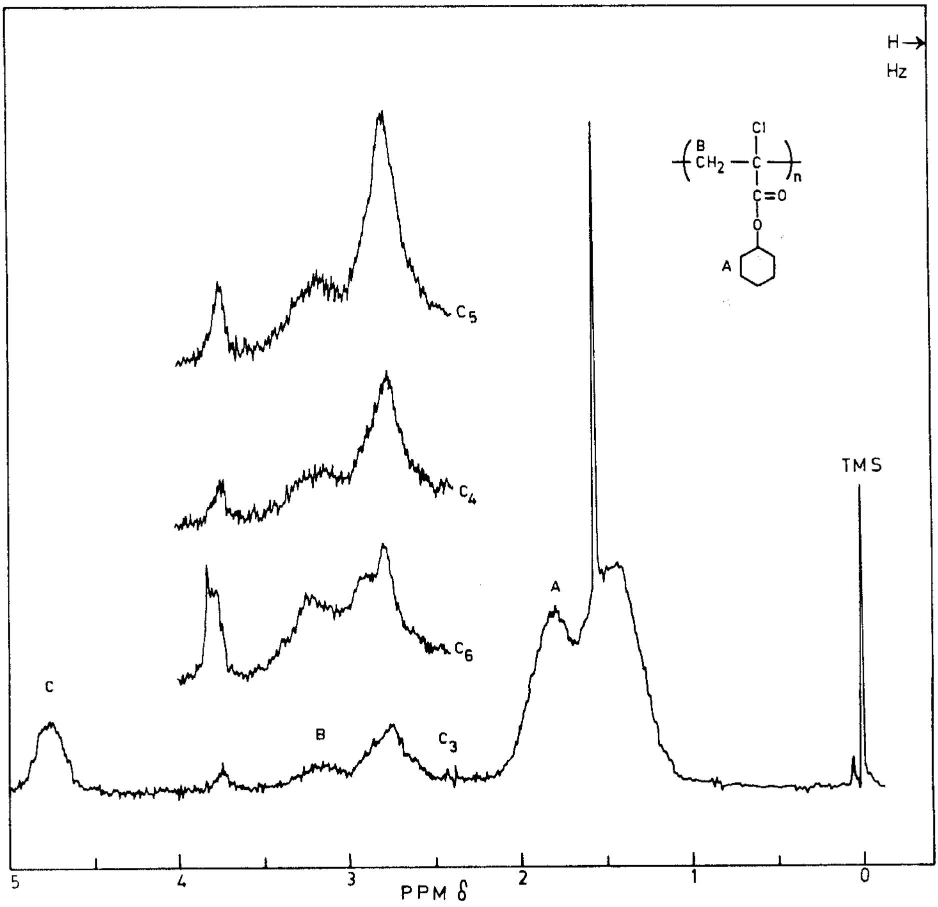


FIG. 2. 100 MHz PMR of poly(cyclohexyl α-chloroacrylate)s synthesized under various conditions (see Table 1). Spectra measured in $CDCl_3$.

molecular weight versus dose (Fig. 3) and are compared with values of other polymers in Table 3. The nonzero G_X value suggests that some crosslinking also takes place. However, the irradiated polymers were soluble in chloroform and THF, indicating that crosslinking is not appreciable. The high G_S value indicates that the polymer predominantly undergoes scission under γ-radiation. The G_S of PCCA is about twice that of poly(methyl methacrylate)

TABLE 2. Molecular Weight of Poly(Cyclohexyl α-Chloroacrylate)

Dose, Mrd	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-6}$	$\overline{M}_w/\overline{M}_n$	$[\eta]_{\mathrm{THF}}$, dL/g
0	1.5	0.35	2.28	0.35
1.2	0.67	0.25	3.73	0.25
2.2	0.88	0.25	2.78	0.25
2.8	0.70	0.22	3.12	0.22

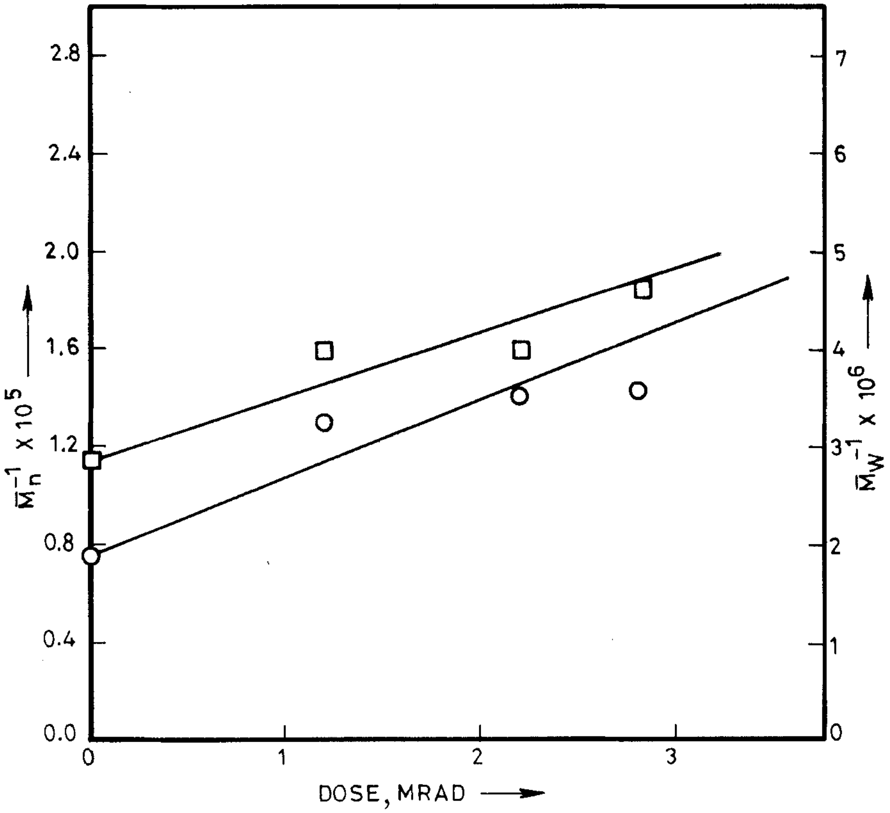


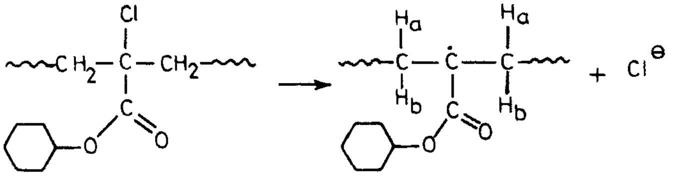
FIG. 3. Variation of reciprocal of number-average (○) and weight-average (□) molecular weight versus dose for poly(cyclohexyl α-chloroacrylate).

TABLE 3. Gamma Radiolysis Yields of Acrylic Polymers

	G_s	G_x
Poly(methyl methacrylate) [1]	1.9	0
Poly(methyl α-chloroacrylate) [2]	7.4	0.9
Poly(2-chloroethyl methacrylate) [3]	0.50	0.08
Poly(cyclohexyl α-chloroacrylate)	3.8	0.6

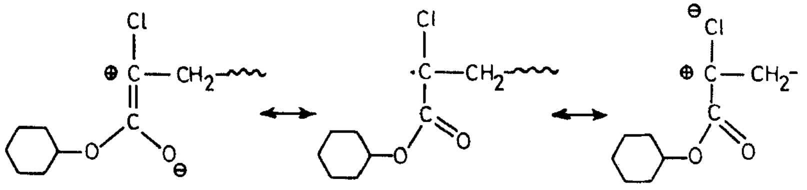
(PMMA), which is considered the standard positive electron beam resist. This may be due to the polar chlorine atom on the backbone, which weakens the carbon-carbon main chain bonds [2]. The G_s value of PCCA is substantially lower than that of poly(methyl α-chloroacrylate) (PMCA). This shows that the alkyl group can affect the G_s value.

The irradiated PCCA (Fig. 4) showed a typical seven-line ESR spectrum, comprised of contributions of two radical species produced by the dissociative electron capture [2]:



Radical I

and



Radical II

A similar seven-line spectrum was reported for PMCA by Babu et al. [2]. The radical yield (G_r) obtained from the ESR spectrum (G_r = 1.80) was

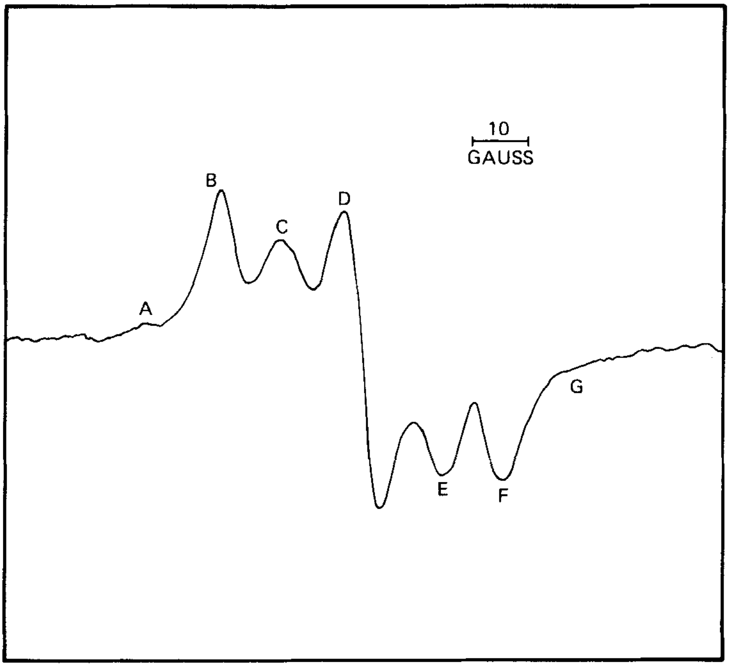


FIG. 4. ESR spectrum of poly(cyclohexyl α-chloroacrylate) after irradiation (dose 1.8 Mrd).

lower than the G_S value. This might be attributed to the annihilation of radicals during the measurements after irradiation.

The IR spectrum of the irradiated polymer was very similar to the unirradiated polymer and without any lactone absorption frequency. This shows that thermal and radiation degradation have different mechanisms. We shall report subsequently on the mechanism of thermal degradation by GC-MS.

ACKNOWLEDGMENT

The authors thank Professor J. C. W. Chien, University of Massachusetts, for providing ESR facilities.

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Received January 16, 1986
Revision received May 27, 1986