

Preparation and characterization of poly(dicyclohexyl itaconate)-*block*-(propylene oxide)

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A series of copolymers of dicyclohexyl itaconate (DCHI) and propylene oxide (PPO) were prepared by using peroxy-carbamates as radical initiators for DCHI. The DCHI content in the copolymers was found to be very similar to that in the feed. The molecular weights of the copolymers prepared showed an inverse relationship with weight per cent of peroxy-carbamates in samples with polydispersities between 1.3 and 2.2. The copolymers were characterized by chemical and physical methods, and their thermal stabilities were tested. The results from thermogravimetric analysis revealed two different thermal decomposition temperatures with two different activation energies. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Segmented, block copolymers of propylene oxide (PPO), mainly due to the possibility of providing a wide range of materials with variable hydrophilic–lipophilic balance (HLB), drew considerable interest in the near past, and already there is an extensive amount of data for this group of polymers. It is a well-established fact that PPO polymers are not water-soluble above a molecular weight of about 500. Block copolymers of dicyclohexyl itaconate (DCHI) and PPO, on the other hand, have not been investigated at all. This copolymer system is of special interest to us. Because the brittle film forming poly-DCHI (PDCHI) cannot be polymerized thermally^{1–3}, there is only a very limited amount of data available for this polymer, and PDCHI is expected to form the vinyl part of the copolymer, which may lead to some interesting properties for the copolymer.

There have been various methods employed for block copolymer formation, such as addition or condensation reactions or even the specific technique of cold mastication, or anionic or group transfer polymerizations^{4,5}. On the other hand, Tobolsky and Rembaum's method, which is based on the preparation of polymeric peroxy-carbamates from low molecular weight rubbery prepolymers⁶, can be used to initiate the radical polymerization of a vinyl monomer. Several papers have been published that describe various modes of preparation and characterization of these copolymers^{7–12}.

In this study, a series of copolymers were first synthesized by preparing peroxy-carbamates (PCs) from

the commercially available low molecular weight dihydroxyl-terminated prepolymers of polypropylene oxide glycol (PPG). PC was used as the radical initiator for the DCHI monomer, which was synthesized from itaconic acid and cyclohexyl alcohol with sulfuric acid as the catalyst. The structures of the copolymers were characterized by spectroscopic, chromatographic and viscometric methods, and their thermal characteristics were examined by d.s.c. and t.g.a.

EXPERIMENTAL

Materials

DCHI monomer was prepared and purified as described earlier¹.

PPG samples (from Fluka A.G.), PPG-1200 and PPG-2000 with molecular weights of 1200 and 2000, respectively, were used after drying *in vacuo* at 70°C for 3 h. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) (from Fluka A.G.) was used without purification. Its purity, as determined by isocyanate analysis, was found as 95.1%.

t-Butyl hydroperoxide (*t*-BHP) (from Fluka A.G.) was distilled under reduced pressure. The peroxide content was found to be 93.3%. It was used after drying over anhydrous magnesium sulfate.

Dibutyltin-dilaurate (T-12) (from Fluka A.G.) was used as a catalyst.

All solvents used in this study were purified according to conventional distillation and drying procedures.

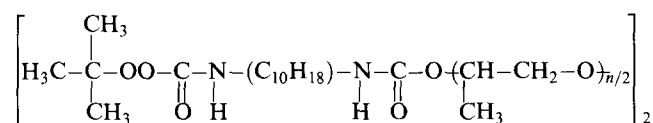
Procedure

Preparation of peroxy-carbamates. The polymeric peroxy-carbamates were prepared in two stages. In the

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first stage, the dried hydroxyl-terminated prepolymers (PPG-1200 and PPG-2000) and the aliphatic diisocyanate (IPDI) were reacted at 80°C in bulk under a blanket of dry nitrogen, for 80 h. The molar ratio of diisocyanate to prepolymer used was 3, in order to prevent undesired chain extensions. The resulting products were decanted with dried petroleum ether in order to separate the excess of diisocyanate. The resulting product was dried at 70°C. The isocyanate content of the end-capped products were determined by the end-group titration of isocyanates¹³, and the experimental results obtained were found to be in good agreement with the theoretically expected values. In the second step, the diisocyanate-terminated urethane was reacted with dried t-BHP in methylene chloride. A few drops of T-12 catalyst was added to the reaction mixture. The reaction was carried out under a dry nitrogen blanket, at room temperature in the dark, for 200 h. The molar ratio of t-BHP to urethane was approximately 3. The resulting peroxy-carbamates were isolated by decanting in petroleum ether and were dried *in vacuo* at room temperature. The molecular weights of the peroxy-carbamates were calculated from their peroxide contents¹⁴, and the decantation procedure mentioned above was repeated until the desired theoretical results were obtained.

The structural formula of the peroxy-carbamates is expected to be



where *n* depends on the molecular weight of PPO.

The preparation conditions and the results of isocyanate and peroxide analysis are all presented in *Table 1*.

Synthesis of copolymers. The peroxy-carbamates prepared, denoted PC-I and PC-II, were used as initiators for the synthesis of copolymers of DCHI. For this, weighed amounts of the peroxy-carbamates were mixed using predetermined amounts of monomer in Pyrex tubes. Toluene was added to the mixture as the polymerization

solvent. The mixtures were then degassed at $1.33 \times 10^{-2} \text{ Nm}^{-2}$, the solutions were distributed into Pyrex tubes and polymerizations were carried out for 300 h at 60°C. The solid products were dissolved in toluene, precipitated in large volumes of methanol, filtered and dried *in vacuo* at 50°C for 48 h.

Characterization. Isocyanate and peroxygen analyses were performed using standard methods^{13,14}.

The molecular weights of copolymers were determined by gel permeation chromatography (g.p.c.) (Waters) and viscometry. In the former technique, tetrahydrofuran (THF) was used as the eluent at 25°C with a flow rate of 1 ml min⁻¹, and molecular weights were calculated with reference to the polystyrene standards. Toluene was used as the solvent at 25°C during the viscosity studies, and molecular weights were calculated by use of the following relationship¹:

$$[\eta] = 13.1 \times 10^{-5} M_V^{0.623} \quad (\text{dl g}^{-1})$$

FTi.r. spectra of the samples were obtained using a Jasco 5300 model spectrometer. PDCHI contents were determined by use of a Shimadzu UV-150-02 model double-beam u.v./vis. spectrometer, based on the determination of the absorbances of pure PDCHI of peroxy-carbamate and of the copolymers at the path length of 229 nm, in cyclohexane⁹.

N.m.r. spectra of the samples were recorded using a Bruker-AC 200L, 200 MHz n.m.r. spectrometer.

Thermal characterization of the samples was done using Shimadzu DSC-41 and TA TGA 951S instruments.

RESULTS AND DISCUSSION

A series of six different molecular weight copolymers of DCHI and PPO were synthesized by use of two peroxy-carbamates with different molecular weights. Related experimental data on the preparation of copolymers are presented in *Table 2*. The method employed for copolymer synthesis in this study is known to yield products that contain a homopolymer of the related vinyl monomer as well. For this reason, the

Table 1 Preparation of peroxy-carbamates

Peroxy-carbamate	Molecular weight of PPG	$\frac{[-\text{NCO}]}{[-\text{PPG}]}$	Isocyanate content (wt%)		Peroxide content (wt%)		M_w^a
			Calculated	Experimental	Calculated	Experimental	
PC-I	1200	3.02	5.1	5.0	3.51	3.54	1810
PC-II	2000	3.00	3.4	3.5	2.44	2.40	2670

^a Molecular weight of peroxy-carbamates found experimentally

Table 2 Characterization of block copolymers

Copolymer	DCHI content (wt%)		Conversion (%)	$[\eta]$ (dl g ⁻¹)	$M_v \times 10^{-3}$ (g mol ⁻¹)	$M_n \times 10^{-3}$ (g mol ⁻¹)	$M_w \times 10^{-3}$ (g mol ⁻¹)	T_g (°C)
	Initial	Found by u.v.						
1	82.6	81.2	92	0.081	30.2	30.7	54.1	112
2	72.2	79.0	61	0.067	22.4	24.5	38.9	109
3	63.5	66.0	34	0.052	14.8	15.5	20.3	106
4	88.2	83.3	63	0.191	120	76.2	167.4	138
5	73.9	69.5	51	0.076	27.2	25.4	40.7	101
6	61.9	60.0	24	0.051	14.6	15.4	20.2	105

Copolymers 1, 2 and 3 were prepared by using PC-I, and copolymers 4, 5 and 6 by PC-II

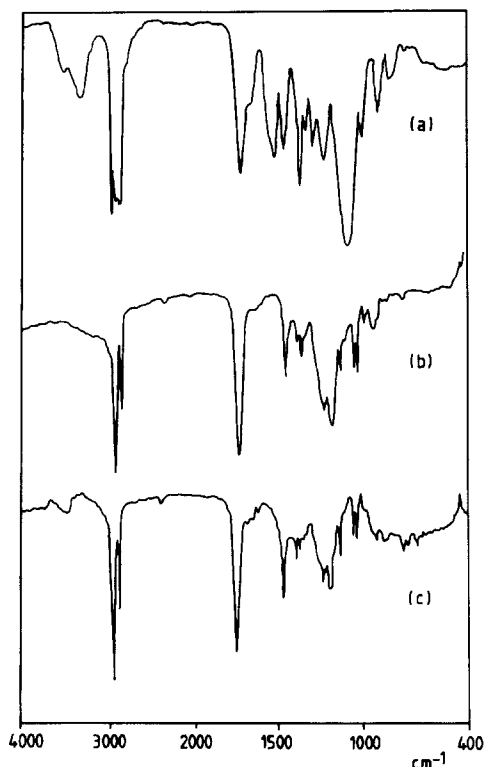


Figure 1 FTi.r. spectra of (a) peroxydicarbamate (PC-I), (b) PDCHI homopolymer and (c) PDCHI-*b*-PPO copolymer 1

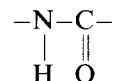


Figure 2 ¹H n.m.r. spectra of (a) prepolymer (PPG-1200), (b) peroxydicarbamate (PC-I) and (c) PDCHI-*b*-PPO copolymer 2

products were also subjected to fractional precipitation⁸. In any case, the weight per cent of homopolymer in the original precipitate was always found to be smaller than 10%, since DCHI monomer cannot be polymerized thermally¹ and the termination step for itaconate ester monomers involves bimolecular termination^{15,16}.

The intermediates and the products were characterized by FTi.r. spectroscopy. In the FTi.r. spectra of the

first-stage capping reaction with diisocyanate, the -OH absorption peaks (at 3520 and 3590 cm⁻¹) disappeared, and the peak at 2280 cm⁻¹ appeared due to the stretching vibration of -NCO (Figure 1). In the second step of the reaction, the disappearance of the -NCO peak obviously indicates the formation of peroxydicarbamate. In the i.r. spectra of the samples, peaks at and near to 3400 cm⁻¹ were observed for all runs, which is due to the -N-H stretching in the peroxydicarbamate



group. This absorption peak indicates the incorporation of the peroxydicarbamate into the copolymer, which provides solid evidence for block copolymer formation. Figure 1 compares the FTi.r. spectra of peroxydicarbamate, PDCHI homopolymer and the copolymer (copolymer 1).

In Figure 2, ¹H n.m.r. spectra of PPG-1200 (prepolymer) PC-I (peroxydicarbamate) and copolymer 2 are presented. As shown in the figure, the signals at 1.10 and 1.13 ppm are due to the -CH₃ groups, while those between 3.08 and 3.65 ppm are from -CH₂ and -CH groups in the prepolymer (Figure 2a). These peaks show small shifts for the peroxydicarbamates: -CH₃ group signals are seen to shift to 1.06 and 1.08 ppm, while -CH₂ and -CH group signals are shifted to the region between 3.32 and 3.57 ppm (Figure 2b). These characteristic macroinitiator signals, which are due to the prepolymer, are also traceable in the n.m.r. spectra of the prepared block copolymers, as shown in Figure 2c, where peaks at 1.13 and 1.16 ppm (for -CH₃) and 3.32–3.60 ppm (for -CH₂ and -CH, respectively) are clearly seen.

The DCHI content of the prepared copolymers as determined by u.v. spectroscopy is also presented in Table 2. The results show that the percentage of DCHI in the copolymers is similar to that in the original mixture. Intrinsic viscosity results and calculated viscosity average molecular weights are also presented in the same table, along with other weight averages. Various molecular weight average values of the copolymer samples were found to lie between 15 000 and 160 000 g mol⁻¹. The viscosities and the number average molecular weights calculated are very close to each other. Polydispersities were found to be between 1.3 and 2.2, as measured by g.p.c.

Another finding, which was expected, is that the molecular weights of the prepared copolymeric samples showed an inverse relationship with the weight per cent of the peroxydicarbamate in the samples, and molecular weights of the samples are seen to decrease with increasing peroxydicarbamate content of the copolymers.

Thermal characterization of samples was done by d.s.c. and t.g.a. D.s.c. thermograms of PPG-1200 prepolymer, the macroinitiator PC-I, block copolymer 3 and the PDCHI homopolymer are illustrated in Figure 3. *T_g* values for the prepolymer and macroinitiator are lower than that for the corresponding copolymers, where two of the *T_g* values corresponding to different blocks are clearly observable. The *T_g* corresponding to PDCHI blocks in the copolymer (copolymer 3) was observed at around 106°C, which is somewhat lower than that of homo-PDCHI (148°C) (Figure 3d), which may indicate the plasticizer effect of PPO blocks on these block

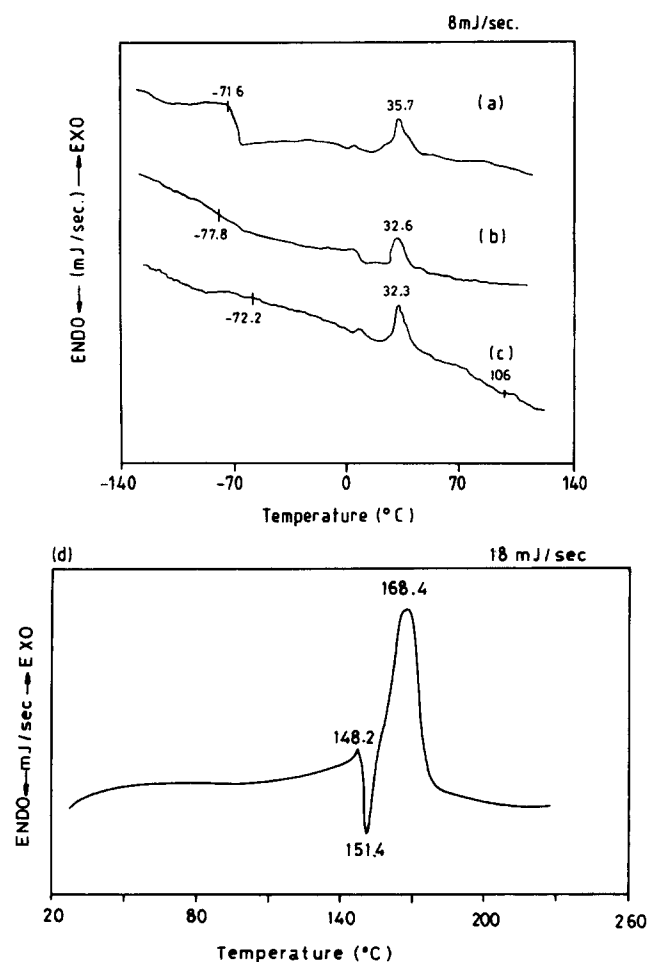


Figure 3 D.s.c. thermograms of (a) prepolymer (PPG-1200), (b) peroxy-carbamate (PC-I), (c) PDCHI-*b*-PPO block copolymer 3 and (d) PDCHI homopolymer

copolymers. The glass transition temperatures for all the block samples are collected in *Table 2*.

The t.g.a. results give an indication of the thermal stabilities of the block copolymers (*Figure 4*). T.g.a. thermograms indicate two thermal decomposition peaks: one around 240°C and the other at around 325°C. Both peaks shift with alteration in the heating rate¹⁷⁻¹⁹ (*Figure 4*). The t.g.a. thermal decomposition results for copolymer 3 for both peaks are given in *Table 3*.

The energy of activations for thermal decomposition can be calculated by using a number of methods, including those of Kissinger and Flynn-Wall, and results for both methods are presented in *Table 4*. The thermal decomposition of the copolymers, as mentioned above, shows two characteristic decomposition temperatures. The lower decomposition temperature has about half of the energy of activation of the main decomposition. Further kinetic investigation of the thermal decomposition results will be the subject of another publication, and will not be included here.

CONCLUSIONS

- (1) A series of copolymers of DCHI and PPO can be obtained by using peroxy-carbamates as radical initiators for DCHI. The DCHI content of the copolymers prepared are very similar to that in the original mixture, with molecular weights between

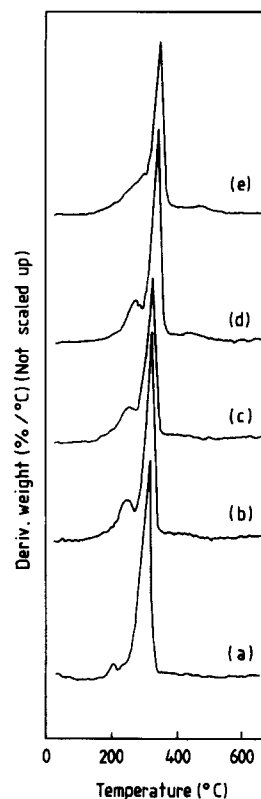


Figure 4 T.g.a. thermograms of (a) PDCHI homopolymer at a heating rate of 5°C min⁻¹, and of PDCHI-*b*-PPO block copolymer 3 at various heating rates: (b) 5°C min⁻¹, (c) 10°C min⁻¹, (d) 20°C min⁻¹ and (e) 30°C min⁻¹

Table 3 T.g.a. thermal decomposition results for copolymer 3

<i>B</i> (°C min ⁻¹)	<i>T</i> _{m1} (°C) ^a	<i>T</i> _{m2} (°C) ^b
5	242.9	325.0
10	248.3	330.7
20	275.5	347.6
30	292.1	354.5

^a Peak 1

^b Peak 2

Table 4 Calculated energies of activation for copolymer 3

Peak	<i>E</i> × 10 ⁻³ (J mol ⁻¹)	
	Kissinger	Flynn-Wall
1	70.8	75.7
2	163.6	165.1

150 000 and 160 000 g mol⁻¹ and polydispersities between 1.3 and 2.2.

- (2) The molecular weights of the copolymer samples prepared have an inverse relationship with the weight per cent of peroxy-carbamate in the samples.
- (3) T.g.a. results revealed the existence of two different thermal decomposition temperatures: the low-temperature decomposition has about half of the energy of activation of the main decomposition.

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