A New Polymeric Peroxycarbamate: Synthesis, Decomposition and Its Use of Polymerization Initiator for Methylstyrene

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ABSTRACT: A new polymeric peroxycarbamate (PPC), having a substituted cycloaliphatic moiety, was synthesized using the corresponding diisocyanate and a dihydroperoxide. The thermal decomposition kinetics of this PPC were studied in 1,4-dioxane solution at 80, 90, and 100°C. The decomposition reaction was found to proceed according to first order kinetics with activation energy of 125 kJ mol⁻¹. Furthermore, this PPC was used to initiate the bulk polymerization of methylstyrene at 80°C and shown to be an effective initiator with negligible chain transfer to the initiator.

KEY WORDS Polymeric Peroxycarbamate / Block Copolymer /
Chain Transfer

Peroxycarbamates (PC) are synthesized by utilising well established techniques of polyurethane chemistry. The polymeric and dimeric PCs were used as free radical initiators in the polymerization and block copolymerization of vinyl monomers.¹⁻³ Block copolymerization is a two-step procedure and involves the sequential decomposition of peroxy linkages introduced in the initiator. We have recently extended⁴ this procedure to cation susceptible monomers such as butyl vinyl ether. In these processes, macroradicals, obtained by the thermolysis of polymeric peroxycarbamates (PPC) or polymers having residual peroxy bonds, are converted to carbocations by the use of organic salts. Although PPCs are efficient multipurpose initiators, chain transfer reactions to the initiator have deterred to the use of these initiators.⁵⁻⁷ Obviously, these reactions lead to the formation of polymers having no peroxy bonds in the main chain and homopolymer formation would be unavoid-

able when used for the synthesis of block copolymers.

In this paper, we describe the synthesis and decomposition kinetics of a new PPC as well as the initiation of methylstyrene polymerization by this initiator, which revealed that transfer to the initiator was negligible.

EXPERIMENTAL

Materials

3-Isocyanatomethyl-3,5,5-trimethyl cyclohexyl isocyanate (IPDI) was a product of Fluka A.G. Its purity, determined by isocyanate analysis, was more than 95%.

2,5-Dimethyl-2,5-dihydroperoxyhexane, (Luperox 2,5-2,5) was supplied by Lucidol Division, Penwalt Corp. It was recrystallised from carbon tetrachloride. The peroxygen content was 98% of the theoretical value.

Dibutyltin dilaurate (Carstan DBTDL, T-12) was a product of Fluka A.G. and was used

as received.

Methylstyrene monomer contained 60% of the *meta*-isomer and 40% of the *para*-isomer. This monomer was successively washed with 10% aqueous NaOH solution and distilled water several times. After drying over calcium chloride, it was fractionally distilled under vacuum.

All solvents were purified according to conventional drying and distillation procedures.⁸

Analyses

Isocyanate analyses were performed by reacting a known amount of material with standard di-*n*-butylamine solution in toluene and back-titrating the excess amine with standard HCl.⁹ The peroxy contents were determined by iodometric methods.¹⁰ IR spectra were recorded on a Perkin Elmer, Model 177 IR spectrometer. GPC chromatograms were obtained using a Knauer M64 instrument and using methylethylketone as the eluent and the flow rate was 1 ml min⁻¹. Molecular weights were calculated according to polystyrene standard samples.

PROCEDURES

Preparation of PPC

15 mmol diisocyanate (IPDI) and 15 mmol dihydroperoxide (Luperox 2,5-2,5) were reacted in 60 ml. dry methylene chloride at room temperature under dry nitrogen atmosphere in the dark for 72 h. The chain extension reaction was carried out in the presence of T-12 catalyst (0.05 g). 15 mmol IPDI was then added to this solution in order to cover both ends of the PC with isocyanate end groups. The reaction was conducted at room temperature for 48 h. The isocyanate end groups were capped with 15 ml isopropanol by reacting for 12 h at room temperature. The product was precipitated by petroleum ether (400 ml), filtered, washed and dried in a vacuum oven at room temperature. Yield, 68.7%; peroxygen content, 11.7%; $\bar{M}_w$ (from the peroxygen content), 1263.5 g mol⁻¹; $\bar{M}_n$ (by a cryoscopic method), 1170.8 g mol⁻¹. The chemical structure of PPC can be represented as follows.

Hydrocarbon backbone in IPDI

Hydrocarbon backbone in Luperox 2,5-2,5

Thermal Decomposition Studies

The thermal decomposition kinetics of PPC were studied in 1,4-dioxane at 80, 90, and 100°C. Weighed amounts of samples were dissolved in the solvent and 10 ml of these solutions were degassed on a high vacuum line

by the freeze-thaw method, sealed and put into a constant temperature bath for the desired time intervals. After the reaction, the tubes were broken, the contents poured into benzene and the amount of unreacted peroxygen determined by iodometric titration.

Polymerization Procedures

Given amounts of PPC and methylstyrene were introduced into pyrex reaction tubes and evacuated in the usual manner. The tubes were then sealed and put into a constant temperature bath at 80°C. At the end of the reaction the mixtures were dissolved in toluene and precipitated in methanol several times. The polymer samples were dried in a vacuum oven. The conversions were deliberately kept below 10% so as to obtain reliable kinetic analysis of the data. The rate, R_p , and average degree of polymerization, $\bar{P}_n$, were calculated from conversion-time data and dilute solution viscosity measurements, respectively. The viscometric equation used was:

$$[\eta] = 7.36 \times 10^{-5} \bar{M}_n^{0.76} \text{ dl g}^{-1} \quad (1)$$

given for benzene solutions at 30°C for poly(methylstyrene) samples.¹¹

RESULTS AND DISCUSSION

The synthesis of PPC was achieved by using a general procedure of polyurethane chemistry. The chain extension reaction was conducted at room temperature in order to prevent the thermal cleavage of the peroxy oxygen bonds. At this step, dibutyltin dilaurate (T-12) was added as catalyst causing a significant increase in the reaction rate. Special care was taken for the removal of unreacted material from the product. IR spectroscopy was routinely used to follow the reactions by monitoring the disappearance of the (NCO) and (OOH) bands at around 2250 and 3520 cm^{-1} and the appearance of (NH) and (C=O) absorptions at around 3440 and 1730 cm^{-1} , respectively. Functional group analysis also confirmed the formation of the predicted structure since the agreement between experimental and theoretical results was fairly good.

The thermal decomposition kinetics of PPC ($10^{-2} \text{ mol l}^{-1}$) were studied by determining the amount of unreacted peroxy oxygen groups as a function of time. First-order plots of $\ln(C_0/C)$

Figure 1. First-order plot for thermal decomposition of polymeric peroxycarbamate: (○), 80°C; (●), 90°C; (□), 100°C.

Figure 2. Arrhenius plot for decomposition rate constant (k_d) of polymeric peroxycarbamate.

versus t for PPC are illustrated in Figure 1, where C_0 and C denote the initial concentration and concentration at time t of the PC groups. The decomposition rate constants (k_d) at 80, 90, and 100°C were calculated from the slopes of those straight lines. The values are $k_d = 1.88 \times 10^{-5}$ (80°C), 5.67×10^{-5} (90°C), and $19.91 \times 10^{-5} \text{ s}^{-1}$ (100°C). The activation energy (E_a) and frequency factor (A) values were estimated to be 125 kJ mol^{-1} and 10^{13} s^{-1} , respectively, from the corresponding Arrhenius plot (Figure 2). The decomposition of PPCs occurs through the cleavage of the labile peroxy oxygen bond. First order decomposition kinetics reveal that there is no induced decomposition as observed⁵ for other type of PPCs. Furthermore, the similar values⁵ of k_d , E_a , and A to other PCs based on aliphatic isocyanates indicates that substitution on the cyclohexyl ring did not have significant effect

Table I. Bulk polymerization of methylstyrene by polymeric peroxydicarbonate

Run No.	Time (min)	$[I]_0 \times 10^4$ (mol l ⁻¹)	$[M]_0$ (mol l ⁻¹)	Yield (wt%)	$R_p \times 10^4$ (mol l ⁻¹ s ⁻¹)	$1/\bar{P}_n \times 10^4$	$\bar{M}_n$
1	250	2.62	7.57	7.18	0.35	1.78	664130
2	240	2.95	7.59	8.55	0.43	2.06	573060
3	150	8.18	7.53	6.67	0.54	2.53	467670
4	180	13.20	7.53	9.48	0.64	3.01	392820
5	100	26.84	7.44	7.35	0.89	3.62	326170
6	70	37.10	7.46	5.52	0.96	3.92	301600
7	60	59.25	7.50	6.05	1.23	4.05	292070
8	50	62.96	7.51	5.29	1.28	4.17	283240
9	71	73.76	7.52	8.11	1.39	4.58	258230
10	80	85.01	7.52	9.73	1.48	5.62	210260

$[I]_0$ = initiator concentration; $[M]_0$ = monomer concentration.

on these parameters.

PPC was utilized as a free radical initiator for the bulk polymerization of methylstyrene at 80°C. Typical results are shown in Table I. Figure 3 illustrates the GPC chromatograms for polymers obtained by using different concentrations of PPC. It is interesting to note that although the molecular weights of the polymers decreased, the polydispersity of the polymers did not change by increasing the PPC concentration in the polymerization indicating the absence of chain transfer to the initiator. Polydispersity values greater than 1.5 may be due to some termination by disproportionation and chain transfer to small molecules such as monomer as suggested by Mutschler *et al.*¹² for *p*-methylstyrene polymerization initiated by AIBN. The radical initiation and polymerization rate is given^{13,14} by:

$$R_i = 2fk_d(I) \quad (2)$$

and

$$R_p = k_p(M)(fk_d(I)/k_t)^{1/2} \quad (3)$$

where (I) and (M) are the initiator and monomer concentrations and k_d , k_p , and k_t are the thermal decomposition, polymerization and termination rate constants, respectively, and f is the initiator efficiency. The term $k_p^2(fk_d/k_t)$ is generally denoted as K^2 , which is a measure of the initiator reactivity. The value of

Figure 3. GPC chromatograms of poly(methylstyrene) obtained by using different polymeric peroxydicarbonate concentrations. PPC (mol l⁻¹) (a), 2.6×10^{-4} ($\bar{M}_w/\bar{M}_n = 2.42$); (b), 8.1×10^{-4} ($\bar{M}_w/\bar{M}_n = 2.32$); (c), 5.9×10^{-3} ($\bar{M}_w/\bar{M}_n = 2.34$); (d), 7.3×10^{-3} ($\bar{M}_w/\bar{M}_n = 2.35$).

K^2 can be obtained from the slope of the plot of R_p^2 versus $(M)^2(I)$ according to eq 3. In this study, the value of K^2 was estimated to be $4.17 \times 10^{-8} \text{ l mol}^{-1} \text{ s}^{-2}$ from Figure 4.

For free radical, bulk polymerization the inverse degree of polymerization ($1/\bar{P}_n$) is given¹³ by:

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2(M)^2} \cdot R_p + C_M + \frac{C_I}{K^2(M)^3} \quad (4)$$

where C_M and C_I represent the chain transfer-to-monomer and chain transfer-to-initiator constants, respectively. If $C_I = 0$, a plot of $1/\bar{P}_n$

Figure 4. Plot of R_p versus $(M)^2(I)$ according to eq 3 for methylstyrene polymerization in bulk at 80°C, initiated by polymeric peroxycarbamate.

Figure 5. Plot of $1/\bar{P}_n$ versus $R_p/(M)^2$ according to eq 4 for methylstyrene polymerization in bulk at 80°C, initiated by polymeric peroxycarbamate.

against $R_p/(M)^2$ should yield a straight line. Such a plot is shown in Figure 5 for PPC initiated methylstyrene polymerization. The straight line obtained, up to the conversions studied, indicates that there is no chain transfer to the initiator. The intercept of this straight line gives C_M . For our system, it was determined to be 8.5×10^{-5} and was in very good agreement with literature values given for polystyrene samples. The values of K^2 and $R_i/(I)$ for the AIBN initiated polymerization of *p*-methylstyrene are $2.5 \times 10^{-8} \text{ l mol}^{-1} \text{ s}^{-2}$ and $4.46 \times 10^{-3} \text{ s}^{-1}$, respectively, as obtained from the data of Munchsler *et al.*¹² It should

be noted that PPC contains more than one labile group. Therefore, dividing the $R_i/(I)$ value obtained for PPC by 6, which is the peroxygen number in PPC, gives a value of 6.27×10^{-6} per decomposing peroxygen bond. The comparison of this value to AIBN indicates that PPC shows slower initiation at 80°C, therefore PPC can be used as an effective high temperature initiator.

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