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A New Method for Investigating the Mechanism of Initiation of Radical Polymerization

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Summary

The mechanism of initiation of polymerization of methyl acrylate by di-*t*-butyl peroxalate at 60°C, has been investigated using 2,2,6,6-tetramethylpiperidine-1-oxyl as a radical trapping agent and isolation of the resulting products. The following processes were identified: Tail addition of *t*-butoxy radicals to monomer, hydrogen abstraction from the methyl group of the monomer and fragmentation of the *t*-butoxy radicals to methyl radicals followed by tail addition of these to the methyl acrylate.

Introduction

The complete understanding of the initiation process in vinyl polymerization is of paramount importance to the polymer chemist, both from the theoretical and from the practical point of view. Although a large body of information is available on the decomposition of various radical initiators, comparatively little is known about the mode of action of the resulting primary radicals on polymerizable monomers. Such a knowledge is indispensable if one is to tailor specific end-groups to polymers and this in turn is of considerable importance since end-groups can have a profound influence on the chemical properties of the polymers.

ESR studies, using the flow technique (FISCHER 1968) and the spin trapping technique (SATO, OTSU 1977), have supplied invaluable information about the mechanism of polymer initiation but in these methods the establishment of unambiguous structures for the radicals is often not possible. This stems from the fact that the initiating entity is usually too far removed from the paramagnetic site to manifest itself in the ESR spectrum. Difficulties also arise in the analysis of complex ESR spectra from mixtures of several radicals and in the detection of species present in a mixture at low concentrations.

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Our aim has been to devise a method for the detection of all the processes taking place in the initiation of polymerization and in particular, a method that would be amenable to the identification of minor pathways. For this, we have developed a technique for trapping transient radicals using stable aminoxyls (nitroxides). These compounds react rapidly and efficiently with carbon-centered radicals giving rise to stable products (alkoxyamines), (ROZANTSEV, SHOLLE 1971) which can be isolated and then identified by the usual techniques of structure determination.

This paper describes the results obtained from the reaction of di-*t*-butylperoxalate with methyl acrylate in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl.

Results and Discussion

The reaction of the di-*t*-butyl peroxalate (DBPOX) with methyl acrylate (MA) in the presence of excess 2,2,6,6-tetramethylpiperidine-1-oxyl (TMPO, **1**) at 60°C, yielded a mixture of compounds **2** , **3** , **4** and **5** in the approximate molar ratio of 85:10:3:2 respectively.

The percentage of **3** in the mixture was estimated by ^{1}H-NMR spectroscopy by comparing the signal intensity of the doubly oxygenated methylene (δ5.47) in **3** with that of the methoxy groups (δ3.6) common to the other components of the mixture. Products **2** and **5** were isolated readily in pure form by column chromatography on silica gel and their percentage of the mixture was determined gravimetrically. Products **3** and **4** were eluted together and their relative ratio measured by ^{1}H-NMR spectroscopy. More careful column chromatography afforded some pure **3** and from the remaining mixture of **3** and **4** , product **4** was isolated following selective hydrolysis of **3** with mild base (**3** being converted to highly polar products) and again chromatography on silica gel. In this way, we secured pure samples of each of the components and determined their relative contribution to the total mixture. The structures of **2**, **3** , **4** and **5** were then established by mass spectrometry and ^{1}H-NMR spectroscopy. For comparison, an authentic specimen of **5** was prepared by the decomposition of acetyl peroxide in benzene at 60°C in the presence of the trapping agent **1** .

In this investigation TMPO (**1**) was chosen as the radical trap because of its ready availability (BRIERE et al. 1965), its high reactivity towards carbon-centered radicals (but not oxygen-centered radicals), its remarkable stability to thermal decomposition and its inertness

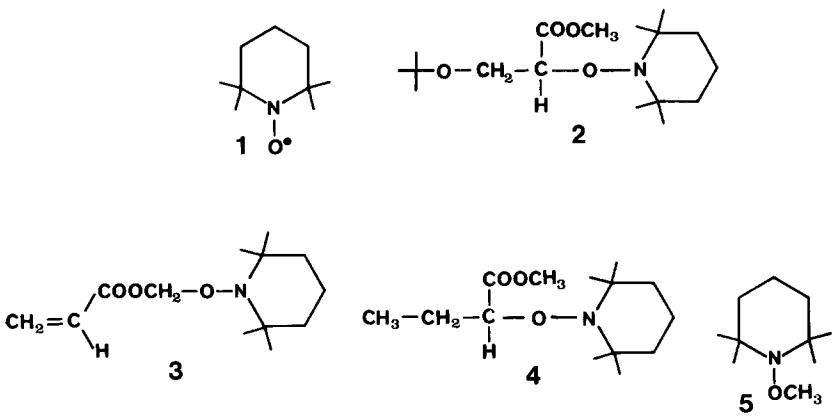
towards even highly reactive monomers. The last two points were clearly evidenced in an experiment in which there was no detectable loss (less than 0.5%) of TMPO (λmax 468 nm) after heating a solution of it in degassed methyl acrylate at 90°C for 24 hrs.

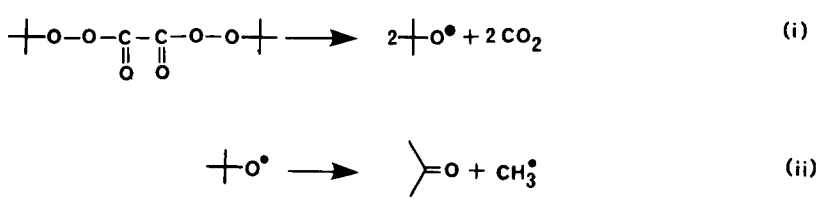
Scheme I outlines the reactions taking place in the system DBPOX-TMPO-MA at 60°C. DBPOX is known to decompose cleanly into *t*-butoxy radicals and carbon dioxide (reaction i) (BARTLETT et al. 1960). The *t*-butoxy radical can undergo β-scission to acetone and a methyl radical (reaction ii) (KOCHI 1973). The extent of this will depend on the temperature of the reaction and the reactivity of the substrate towards the *t*-butoxy radical. Highly reactive substrates and low temperatures will minimize the extent of the β-scission reaction (ii).

Under the conditions of our experiment, the *t*-butoxy radical reacts mainly by a "normal" tail-addition to the monomer giving rise to radical **6** which is then trapped by TMPO resulting in product **2** (reaction iii). Products **4** and **5** clearly show the presence of the methyl radical (reactions v and vi) and it is of interest to note that the methyl acrylate competed with the aminoxyl for the methyl radical whereas radicals **6**, **7** and **8** reacted exclusively with the trapping agent. Products containing more than one monomer unit were not detected.

The most significant aspect of the present investigation has been the isolation and identification of product **3**. This would arise by way of a hydrogen abstraction from the methyl group of the monomer (reaction iv) and of the two radicals (methyl and *t*-butoxy) derived from DBPOX, the *t*-butoxy is the more likely one to be involved in hydrogen abstraction (KOCHI 1973). This suggests that in the polymerizations of acrylic esters with *t*-butoxy radicals, some polymer chains will most likely be initiated or terminated by groups of the type CH_2=CRCOOCHR. Furthermore, the observation that reaction iv competes with double-bond addition (reaction iii) suggests that hydrogen abstraction could also take place from the alkyl groups of polymerized acrylic esters resulting in branching of the polymer, especially in polymerizations carried out to high conversion. This aspect of the work is now under further investigation and the results will be reported elsewhere.

The advantages of the trapping technique described herein is evident from other results reported to date. In a study of the reaction of *t*-butoxy radicals with monomers, only the double-bond addition to MA (reaction





scheme I

iii) was detected by ESR using the spin trapping technique with 2-methyl-2-nitrosopropane (SATO, OTSU 1977). The determination of *t*-butanol, derived from the *t*-butoxy radical, demonstrates the importance of hydrogen abstraction from acrylic esters but the exact nature of the radical species involved cannot be deduced from these experiments (ENCINA et al. 1978 and RIZZARDO, SOLOMON 1979).

A detailed study of the reaction of a number of initiator radicals with a variety of vinyl monomers is now underway and the results of these will be published in the future.

Experimental

Di-*t*-butyl peroxalate (DBPOX) was prepared by the reaction of oxalyl chloride with *t*-butyl hydroperoxide (BARTLETT et al. 1960). 2,2,6,6-Tetramethylpiperidine-1-oxyl (TMPO) was obtained from the oxidation of 2,2,-6,6-tetramethylpiperidine with hydrogen peroxide in the presence of phosphotungstic acid (BRIERE et al. 1965). Methyl acrylate was purified by fractional distillation at reduced pressure.

^{1}H-NMR spectra were obtained with a Varian HA100 spectrometer using carbon tetrachloride as the solvent and TMS as the internal standard. Chemical ionization mass spectra were recorded with a Finnigan 3300F instrument employing methane as the reagent gas.

The radical trapping experiment and the isolation of the products were carried out as follows: A solution of DBPOX (0.23g) and excess TMPO (approx. 0.5g) in methyl acrylate (80 ml) was degassed by repeated freezing and thawing on a vacuum line and then placed in a constant temperature bath at 60°C for 1 hr. Most of the DBPOX would have decomposed during this time since its half-life at 60°C is approximately 7 minutes (BARTLETT et al. 1960). The solvent was removed at reduced pressure and the residue chromatographed on silica gel (150-230 mesh, 40g). Elution with cyclo-hexane-diethyl ether (49:1) gave product **5** (6 mg), identical with an authentic sample prepared by the decomposition of acetyl peroxide in the presence of excess TMPO in benzene at 60°C.

Products **3** and **4** were obtained as a mixture (62 mg) on further elution of the silica gel column with the same solvent system. The molar ratio of product **3** to product **4** was determined to be approximately 3.5:1 by ^{1}H-NMR spectroscopy.

Continued elution of the silica column with cyclohexane-diethyl ether (49:1) afforded product **2** (0.53g). m/e 316 (M+1). NMR (CCl_4, δp.p.m.): $CH_2C\underline{H}$, 4.26, 4-line signal; $C\underline{H}_2CH$, 3.68-3.36, complex signal (CH_2CH form an ABC system since the CH_2 is adjacent to a chiral center and its protons are non-equivalent); OCH_3, 3.62, singlet; remaining 21 protons, 1.55-0.95.

Further elution of the silica column yielded only TMPO, employed in excess in the trapping experiment.

The mixture of products **3** and **4** isolated above, was rechromatographed on silica gel (30g). Elution with cyclohexane-diethyl ether (99:1) gave product **3** (22 mg). m/e 242 (M+1). NMR (CCl_4, δp.p.m.): CH_2=CH, 6.6-5.7, 12-line pattern consistent with ABC system; OCH_2O, 5.47, singlet; remaining 18 protons, 1.6-1.0.

Further elution of this chromatographic column again gave products **3** and **4** as a mixture. This was dissolved in CD_3OD (0.3 ml) in an NMR tube and treated stepwise with a dilute solution of KOH in D_2O. The rapid hydrolysis of product **3** (less hindered and more reactive ester group) was followed by NMR spectroscopy. When the hydrolysis of **3** was complete the solution was acidified with two drops of acetic acid and the solvent was removed at reduced pressure. The residue was extracted with benzene and the benzene solution passed through a short column of silica gel. The eluent contained pure **4** (12 mg). m/e 258 (M+1). NMR (CCl_4, δp.p.m.): $CH_2C\underline{H}$, 4.10, triplet, J=7Hz; OCH_3, 3.63, singlet; $CH_3C\underline{H}_2CH$, 1.8, multiplet; $C\underline{H}_3CH_2$, 0.84, triplet J=7Hz; remaining 18 protons, 1.55-0.9.

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