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Effects of 1,2,3-triphenylcyclopropene on radical polymerizations

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Summary

1,2,3-Triphenylcyclopropene (TPCP) is a powerful retarder for polymerizations of methyl methacrylate (MMA) and styrene initiated by benzoyl peroxide or azobisisobutyronitrile. End-groups in polymers of MMA were studied by 13C-NMR spectroscopy and also, in the case of the peroxide, by using radioactive initiator. It was shown that, towards the benzoyloxy and 1-cyano-1-methylethyl radicals, the reactivity of TPCP exceeds that of MMA by factors of about 60 and three respectively at 60°C. TPCP can be used to introduce into polymers end-groups of special types.

Introduction

It has been demonstrated that the E-isomers of stilbene and related compounds are very reactive towards the benzoyloxy radical (1) derived from thermal dissociation of benzoyl peroxide (BPO). The various compounds were used as minor constituents of systems in which a monomer, usually methyl methacrylate (MMA), was polymerized at 60°C using BPO as initiator. The high reactivity of an additive towards the benzoyloxy radical was demonstrated by showing that polymers prepared in its presence contained substantial numbers of benzoate end-groups attached to units derived from the additive.

In one method of working, BPO containing tritium in its rings and carbon-14 in its carbonyl groups (ra-BPO) was used so that the numbers of benzoate and phenyl end-groups could be compared for the polymers. A reactive additive increased the proportion of the ester end-groups and it was possible to compare k, k' and k" which are the rate constants respectively for the decarboxylation of the benzoyloxy radical, its attachment to the monomer and its attachment to the additive. In an alternative procedure, BPO was enriched with carbon-13 in its carbonyl groups (13C-BPO) and the derived polymers were examined by 13C-NMR. The chemical shift for the enriched carbonyl carbon in a benzoate end-group depends upon the nature of the attached unit; it was possible to compare the numbers of benzoate groups adjacent to units derived from the monomer and the additive and then to find k"/k' directly without involvement of k.

Both procedures have been used for polymers prepared from MMA in the presence of a low concentration of 1,2,3-triphenylcyclopropene (TPCP). The effects of the additive on the rate of polymerization and upon that of styrene (STY) were studied dilatometrically. In some cases, azobisisobutyronitrile (AIBN) replaced BPO as initiator. AIBN enriched with carbon-13 in its nitrile groups (13CN-AIBN) was used in an attempt to detect 1-cyano-1-methylethyl end-groups joined to units derived from TPCP and to compare the rate constants for the additions of the 1-cyano-1-methylethyl radical to MMA and TPCP.

Some experiments were performed with trans stilbene oxide (STO) as an

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additive instead of TPCP. Rates of polymerization were measured and ra-BPO was used to discover whether the olefin oxide showed appreciable reactivity towards the benzoyloxy radical.

Experimental

The preparations of the isotopically enriched or labelled initiators have been described already (2,3,4). TPCP (Lancaster Synthesis) and STO (Aldrich) were purified by recrystallization; other materials were purified by standard procedures. Polymerizations were performed in the absence of air using initiator at about 1 x 10^{-3} mol/dm^3. They were followed dilatometrically and conversions were limited to 10%. Polymers were recovered by precipitation in methanol and purified by two further precipitations, usually from solutions in toluene; they were finally dried in vacuum.

Radioactive materials were assayed by scintillation counting of solutions using a Wallac 1219 "Spectral" counter; specific activities are quoted in Bq/g. 13C-NMR spectra were recorded on a JEOL GSX-400 spectrometer operating at 100 MHz.

From the specific activities of the peroxide and a derived polymer, a fraction $\underline{x}$ given by (no. of benzoate end-groups)/(sum of nos. of benzoate & phenyl end-groups) is calculated by means of equation (i)

$$\underline{x} = \frac{{}^{14}\text{C-activity of polymer}}{{}^{14}\text{C-activity of peroxide}} \times \frac{{}^{3}\text{H-activity of peroxide}}{{}^{3}\text{H-activity of polymer}} \qquad \text{(i)}$$

When MMA is polymerized in the presence of an additive, A, equation (ii)

$$\frac{\underline{x}}{1-\underline{x}} = \frac{k'[\text{MMA}]}{k} + \frac{k''[\text{A}]}{k} \qquad \text{(ii)}$$

is used to calculate k"/k, taking k'/k as 0·31 dm^3/mol.

When some 13C-enriched benzoate groups are attached to units derived from MMA and others to units derived from A, and the two types of end-group give rise to separate NMR signals, equation (iii) can be applied for determination of k"/k'.

$$\frac{\text{spectral area for Ph.CO.O.A- groups}}{\text{spectral area for Ph.CO.O.MMA- groups}} = \frac{k''[\text{A}]}{k'[\text{MMA}]} \qquad \text{(iii)}$$

Results

TPCP is a powerful retarder for the polymerizations of MMA and of STY initiated by either BPO or AIBN (see Figure 1). The magnitudes of the effect are similar for the two monomers and both initiators.

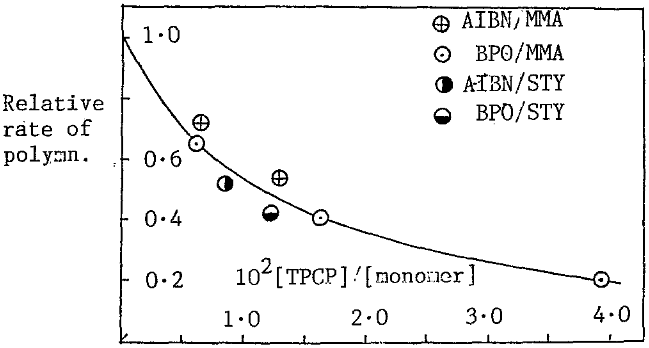

Figure 1. Effects of TPCP on rates of radical polymerizations at 60°C.

Polymerizations of MMA in toluene at 60°C, using ra-BPO as initiator and TPCP as additive, are referred to in Table 1. Application of equations (i) and (ii) leads to the shown values of $\underline{x}$ and k"/k; from the values of the latter quantity and that for k'/k, it is deduced that k"/k' is about 74.

Table 1. Experiments involving radioactive benzoyl peroxide

(concns. in feed)/ (mol/dm^3)		(spec. acts. of polymer)/ $(10^2$ Bq/g)			(k"/k)/
[MMA]	10^2[additive]	tritium	carbon-14	$\underline{x}$	(dm^3/mol)
3·10	3·48 (a)	3·24	1·58	0·634	22
2·95	1·83 (a)	3·18	1·41	0·575	24
3·10	9·49 (b)	6·20	0·83	0·487	*

* see text

(a) TPCP; 10^{-5} (spec. acts. of BPO) :- ^{3}H, 6·37; ^{14}C, 4·90.

(b) STO ; 10^{-5} (spec. acts. of BPO) :- ^{3}H, 10·44; ^{14}C, 2·87.

Figure 2 shows the 13C-NMR spectrum of a sample of polyMMA prepared using 13C-BPO in a system in which [TPCP]/[MMA] was 1·97 x 10^{-2}. The prominent signals near 166 ppm are those expected for benzoate groups joined to units derived from MMA. They are accompanied by a number of small signals between 163·7 and 165 ppm, attributed to benzoate groups adjacent to units derived from TPCP. Integration of the small signals is not very reliable but the value of the ratio of the spectral area for "MMA end-groups" to that for "TPCP end-groups" is approximately 0·87; from application of equation (iii), k"/k' is 59.

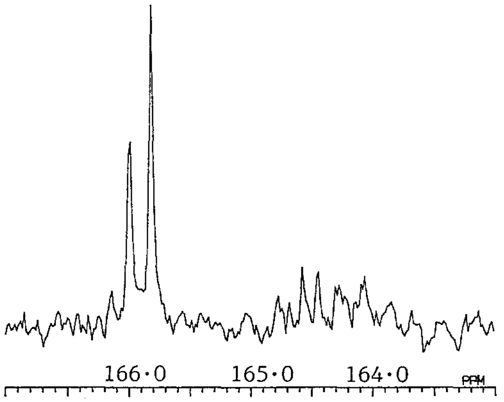

Figure 2. 100 MHz 13C-NMR spectrum of polyMMA prepared using 13C-BPO in the presence of TPCP. For other details, see text.

13CN-AIBN was used as initiator at 60°C in a system in which [MMA] and [TPCP] were 2·28 and 0·23 mol/dm^3 respectively; an identical polymerization was performed with unenriched AIBN. The reactions were slow and the resulting polymers had low molecular weights. In both cases, the final purification of polymer was achieved by precipitation in methanol of a solution of the polymer in ethyl acetate instead of toluene so that any "aromatic" signals in the 13C-NMR spectrum of the polymer could not have been caused by retention of traces of solvent.

The 13C-NMR spectrum of the polymer made with enriched AIBN (see Fig. 3b) showed prominent signals at ca 125 ppm as expected for 1-cyano-1-methylethyl end-groups attached to units derived from MMA (see Figure 3a). Additional smaller signals between 125·5 and 132 ppm could have corresponded to initiator fragments attached to units formed from TPCP and/or to the aromatic carbons contained in any TPCP incorporated in polymer. The molecular weight of the polymer was so low that signals arising from the unenriched methyl groups in initiator fragments were evident at ca 25·5 and 30 ppm (see Figure 3c); there was however structure absent from the signals arising from the methyl carbons in end-groups in polyMMA prepared using AIBN enriched in its methyl groups (13Me-AIBN) but in the absence of TPCP. There was imbalance between the two sets of methyl resonances and the area covered by the signals around 30 ppm in Figure 3c was 1·64 times that for those around 25·5 ppm.

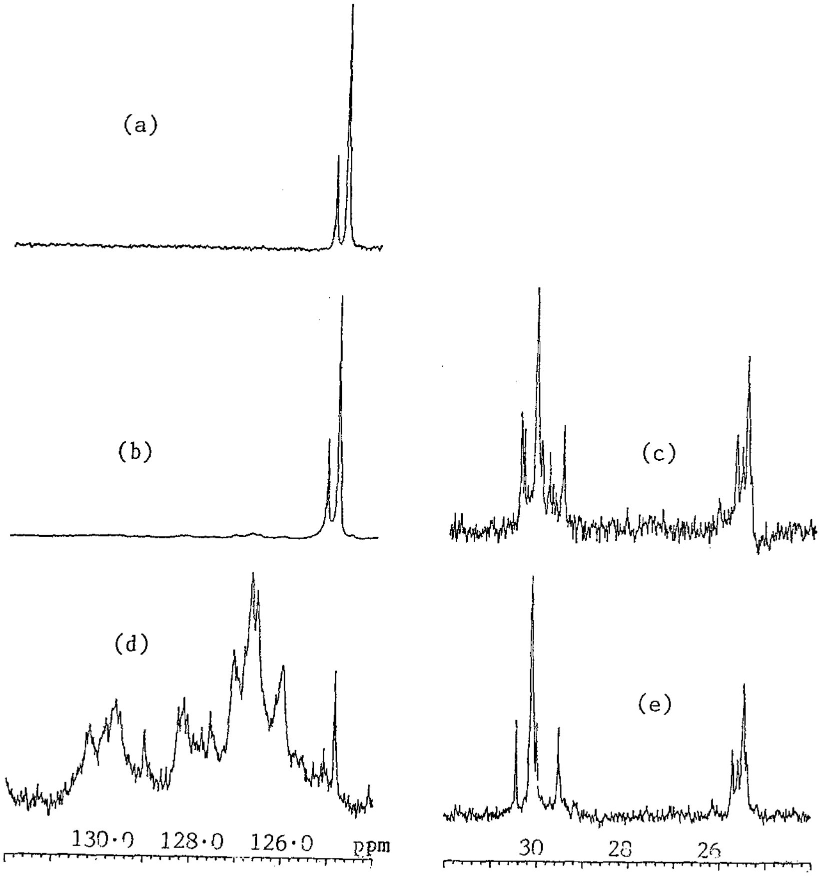

Figure 3. Parts of 100 MHz 13C-NMR spectra of samples of polyMMA.
(a) Initiation by 13CN-AIBN.
(b) & (c) Initiation by 13CN-AIBN in the presence of TPCP.
(d) & (e) Initiation by unenriched-AIBN in the presence of TPCP.
For other details, see text.

The NMR spectrum of the polymer made with unenriched AIBN and TPCP had peaks due to the methyl and nitrile carbons in initiator fragments. The signals from the methyl carbons (see Figure 3e) matched those in Figure 3c and the area for the signals near 30 ppm was greater than that for the signals near 25·5 ppm by a factor of 1·62. There is therefore no indication that the spectrum in Figure 3c was affected by coupling between 13C-nuclei in enriched nitrile groups and those in unenriched methyl groups. The imbalance between the two sets of methyl resonances is attributed to initiator fragments attached to TPCP units and the spectral areas corresponding to end-groups attached to TPCP and MMA are taken as being in the ratio 0·63:2. Application of an equation analogous to (iii) indicates that the rate constant for the reaction of TPCP with the 1-cyano-1-methylethyl radical at 60°C is 2·9 times that for the corresponding reaction involving MMA. The signals between 124 and 132 ppm in Figure 3d include those near 125 ppm arising from unenriched nitrile carbons in end-groups joined to MMA units; the remaining signals must include a small contribution from initiator fragments attached to TPCP units but the main contribution must be due to the aromatic carbons in TPCP units each of which has 18 such carbons.

STO, at concentrations up to at least that corresponding to [STO]/[MMA] = 2·6 x 10^{-2}, had very little effect on the rate of polymerization of MMA with either BPO or AIBN as initiator. The experiment involving MMA,STO and ra-BPO (see Table 1) led to a small negative value for k"/k. If experimental error had caused the quoted value of x to be lower than the true value by as much as 4%, then k"/k would have been 0·66 dm^3/mol corresponding to the reactivity of STO towards the benzoyloxy radical being about twice that of MMA. It is clear therefore that STO is certainly much less reactive than TPCP towards the radical.

Discussion

The results of experiments involving ra-BPO and of that in which 13C-BPO was used indicate that TPCP is very reactive towards the benzoyloxy radical although agreement between the values for k"/k' appears not to be good. It has been stated already that integration of the NMR spectrum may have been unreliable. It must also be noted that the results obtained using ra-BPO are subject to error; the value of $x/(1-x)$, used in application of equation (ii), is very sensitive to small changes in x which is found from measurements of four specific activities. It is plain that TPCP is more reactive, by a factor probably of at least 1·25, towards the benzoyloxy radical than the E-isomer of stilbene which is about 48 times as reactive as MMA.

It is likely that the first product from the interaction of TPCP with an initiating radical R· is the adduct  $\mathrm{R.CPh\text{-}\dot{C}Ph}$ (bridged by CHPh) but ring-opening most probably occurs very readily to give the substituted allyl radical $\mathrm{R.CPh{:}CPh.\dot{C}HPh}$ or its alternative $\mathrm{R.\dot{C}Ph.CPh{:}CHPh}$. Low reactivity of this stabilized allylic radical would account for TPCP being an effective retarder of polymerization; some of the radicals might fail to react with monomer and instead might engage in a process resembling primary radical termination. If all the radicals are consumed either in reaction with monomer or in termination by combination, the procedures for assessing the reactivities of TPCP towards the benzoyloxy and 1-cyano-1-methylethyl radicals are not invalidated; loss of the radicals, including any not entering polymer as a result of terminating by disproportionation, would however lead to an underestimate of the reactivity of TPCP.

The complexity of the 13C-NMR signals arising from benzoate groups attached to units derived from TPCP can be explained by the existence of various structures for those units, as shown in the preceding paragraph. Further complications can be caused by geometrical isomerism and the presence of chiral centres; in addition, some TPCP units may be joined to the tails of MMA units and others to the heads, depending on whether the Ph.CO.O.TPCP· radical reacts with monomer in a growth reaction or with a polymer radical in a termination process. It is clear that the presence of TPCP in a polymerizing system leads to the formation of polymers having unusual structures near some of the end-groups; these structures include some in which phenyl groups are placed on three adjacent carbon atoms.

It must be accepted that polyMMA radicals and also phenyl radicals, produced from those benzoyloxy radicals which undergo decarboxylation, may react with TPCP; these processes would contribute to the observed retardation. The reaction of TPCP with the growing radicals cannot occur as readily as its reaction with the benzoyloxy radicals otherwise systems, for which the initial values of [MMA]/[TPCP] were in the region of 100, would not produce polymers of molecular weight sufficient for them to be precipitated in methanol. This conclusion is borne out by the finding that,although TPCP is more reactive than MMA towards the carbon-centred 1-cyano-1-methylethyl radical, the factor is only about three; a similar value is likely to apply to their relative reactivities with respect to the polyMMA radical.

Many olefin oxides undergo ring-opening polymerization by ionic mechanisms (5) but there appears to be no report of them polymerizing in that way by a radical mechanism (6). The low reactivity of STO towards the benzoyloxy radical is therefore not surprising.Further, the structure of STO only partially satisfies the requirements for high reactivity towards that radical; the carbon atom to which the radical might become attached carries an aromatic group but there is not extensive conjugation through the molecule. These conditions are met by 1,2,3-triphenylcyclopropene, as they are by stilbene-like compounds Ar.CH:CH.Ar and by 1,4-diaryl-1,3-butadienes Ar.CH:CH.CH:CH.Ar (7).

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