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The involvement of 1,6-diphenyl-1,3,5-hexatriene and 1,8-diphenyl-1,3,5,7-octatetraene in the radical polymerization of methyl methacrylate

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Summary

The α,ω-diphenyl derivatives of 1,3,5-hexatriene and 1,3,5,7-octatetraene strongly retard the radical polymerization of methyl methacrylate (MMA); the effects are greater when initiation is achieved with benzoyl peroxide than when azobisisobutyronitrile is used. The tetraene and the triene are respectively 575 and not less than 240 times as effective as MMA in capturing the benzoyloxy radical at 60°C.

Introduction

1,4-Diphenyl-1,3-butadiene (DPB) is very effective in capturing the benzoyloxy radical (1); the rate constant for the reaction at 60°C is about 250 times that for the addition of the radical to methyl methacrylate (MMA). Very high reactivity towards the benzoyloxy radical has been found also for other 1,4-diaryl derivatives of 1,3-butadiene (2). The study has now been extended to α,ω-diphenyl derivatives of other conjugated polyenes viz. 1,6-diphenyl-1,3,5-hexatriene (DPHX) and 1,8-diphenyl-1,3,5,7-octatetraene (DPOC).

Experimental

Most of the experimental procedures and methods of calculation have been described previously (1). DPHX and DPOC (Aldrich) were recrystallized from toluene, giving products with sharp melting points. The purities were confirmed by the fact that the materials gave single peaks when examined by GPC using standard equipment operating with tetrahydrofuran and PL gel columns specified as having pores of 500 Å and 100 Å; a refractive index detector was used and calibration was performed with polystyrene standards.

MMA containing either DPHX or DPOC at low concentration was polymerized in dilatometers with toluene as diluent under air-free conditions at 60°C using either benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) as initiator. In some experiments, use was made of BPO enriched fiftyfold at the carbonyl sites with carbon-13 (^{13}C-BPO) and in others the peroxide was labelled in the rings with carbon-14 (^{14}C-BPO). AIBN labelled in the methyl groups with carbon-14 was used in some cases.

Conversions based on MMA did not exceed 10%. Polymers were recovered by precipitation in methanol, purified by two further precipitations from solutions in toluene and finally dried in vacuum. The specific activities of ^{14}C-labelled initiators and the derived polymers were measured by scintillation counting of solutions. The ^{13}C-NMR spectra of polymers prepared using ^{13}C-BPO were recorded at 100 MHz (carbon-13) on a JEOL GSX-400 spectrometer with $CDCl_3$ solutions and using a 5 mm. probe.

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Results

DPHX and DPOC were found to be powerful retarders for the polymerization of MMA; when using monomer at 2.90 mol dm^{-3} with BPO, the concentrations of the triene and the tetraene required to reduce the rate by 50% were 0.28 x 10^{-2} and 0.10 x 10^{-2} mol dm^{-3} respectively i.e. considerably less than the corresponding concentration (2.90 x 10^{-2} mol dm^{-3}) for DPB. Retardation was less marked for polymerizations initiated by AIBN instead of BPO; the concentrations of DPB, DPHX and DPOC needed to halve the rate of polymerization were 4.60 x 10^{-2}, 0.38 x 10^{-2} and 0.19 x 10^{-2} mol dm^{-3} respectively.

Rates of polymerization were reproducible when reaction mixtures were made using solid DPHX but not when using aliquots of a standard solution in toluene. The extent of retardation became smaller with lengthening of the time for which the solution had been stored at room temperature with access to the air; the effect was noticeable after 24 hours. Examination by GPC confirmed that the solid DPHX was of quite high purity even after storage for about a year; it showed however that much of the triene was converted into material of higher molecular weight during storage at about 20°C in solution of concentration 3 x 10^{-2} mol dm^{-3} for six weeks and that the change was nearly complete after standing for 26 weeks (see Figure 1). Similar experiments involving DPOC showed that deterioration in solution was very much less evident than for DPHX. An air-free solution of DPHX in toluene was stored at 60°C for 21 hours; use of GPC showed that only quite a small proportion of the triene was changed into material of higher molecular weight (see Figure 1). It is evident that the product formed from DPHX has lower reactivity towards radicals than the parent substance.

The specific activity of polyMMA prepared from monomer at 2.90 mol dm^{-3}

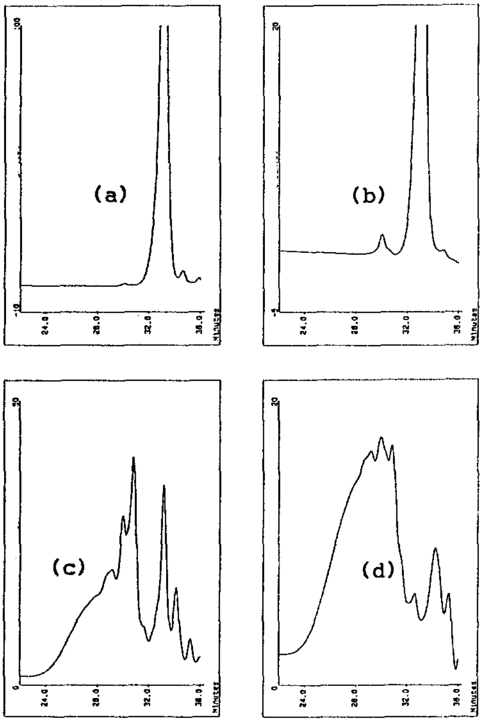


Figure 1. Gel permeation chromatograms for DPHX.
(a) fresh solution;
(b) solution stored for 21 hours at 60°C in absence of air;
(c) solution stored for 6 weeks in air at room temperature;
(d) as for (c) but storage for 26 weeks.
Ordinates show detector response.

with ^{14}C-BPO at 0.80×10^{-2} mol dm^{-3} and that of the polymer derived from a similar system containing also DPHX at 0.46×10^{-2} mol dm^{-3} were 5.57×10^{2} and 1.87×10^{3} Bq g^{-1} respectively; the corresponding quantity for the peroxide itself was 8.50×10^{5} Bq g^{-1}. Application of the relationship

(specific activity of polymer) = 121(specific activity of peroxide)/100n

where n is the number of MMA units incorporated for each initiator fragment gives values of 1850 and 550 for n in the products from the unretarded and retarded polymerizations respectively, assuming that incorporation of DPHX in the latter case was only slight. The rate of the retarded polymerization was 30% of that of the unretarded process so that values of (relative rate)/n were 0.545×10^{-3} and 0.541×10^{-3} respectively. The closeness of the two values shows that DPHX did not affect the rate of entry into polymer of initiator fragments derived from BPO. A similar conclusion was reached for the fragments formed from AIBN, as a result of experiments with azonitrile labelled with carbon-14.

Figure 2 shows parts of the ^{13}C-NMR spectra of polymers of MMA made using ^{13}C-BPO in the presence of either DPHX or DPOC; the polymerizations lasted 24 hours. In both spectra, the two rather sharp peaks near 166 ppm are characteristic of ^{13}C-enriched benzoate groups attached to MMA units. The neighbouring signals must be attributed to isotopically enriched benzoate groups joined to units derived from the additive; for the polymer prepared with DPHX, these signals are well defined but they are very broad for the polymer made in the presence of DPOC.

For the system involving DPHX, (spectral area for Ph.COO.DPHX-)/(spectral area for Ph.COO.MMA-) is 0.90; the value of [DPHX]/[MMA] in the feed

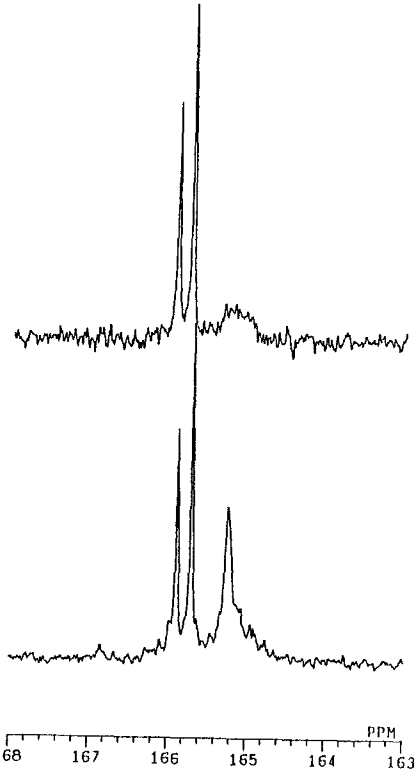
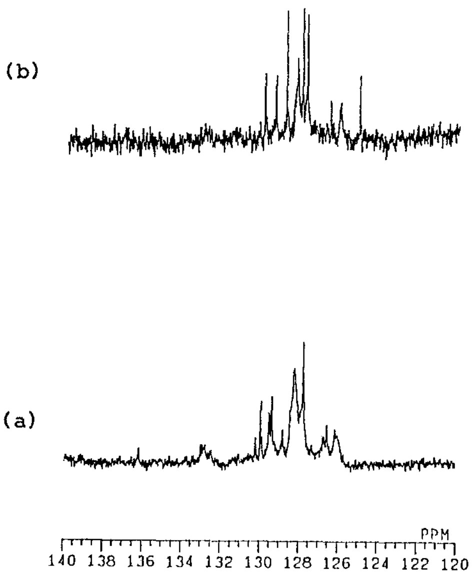


Figure 2. Parts of the ^{13}C-NMR spectra of samples of polyMMA prepared using ^{13}C-BPO in the presence of (a) DPHX (b) DPOC; for further information, see text.



was 0.37×10^{-2}. Taking k_2 and k_2' as the rate constants for the attachment of the benzoyloxy radical to MMA and DPHX respectively, k_2'/k_2 is obtained as $0.90/(0.37 \times 10^{-2})$ i.e. 243. The results of the tests involving GPC show that some of the triene originally present must have changed into material of lower reactivity during the making of the polymer so that the effective value of [DPHX]/[MMA] must have been less than the initial value and the value of 243 for k_2'/k_2 must be regarded as a lower limit. For the polymer prepared in the presence of DPOC, the corresponding ratio of spectral areas is 0.46; [DPOC]/[MMA] had an initial value of 0.80×10^{-3} and there seems to be no need to consider loss of DPOC during the polymerization. For the tetraene, k_2'/k_2 is obtained as 575.

Small but distinct signals between 125 and 133 ppm in the spectra of Figure 2 must be attributed to carbon atoms in phenyl or olefinic groups. For the polymer made in the presence of DPHX and that prepared using DPOC, the signals cover areas respectively 2.0 and 1.3 times those covered by the corresponding signals arising from the enriched carbonyl sites in benzoate end-groups. The lack of sensitivity for these minor signals precluded the recording of spectra under conditions which would eliminate the nuclear Overhauser enhancement. As a result, the contribution to spectral areas of protonated carbons is effectively increased, relative to that from carbonyl carbons, by a factor of up to three with a likely factor of about two. The ratios of spectral areas can therefore properly be modified from 2.0 and 1.3 to approximately 1.0 and 0.6 for the cases of DPHX and DPOC respectively.

Discussion

The retarding effects of the polyenes are explained by supposing that reaction of an initiating radical or a growing polymer radical with a polyene produces a radical so stabilized that it does not react readily with monomer and may engage in termination processes. Differences between the retarding effects for polymerizations initiated by BPO and AIBN indicate that retardation is, in part at least, connected with reactions involving radicals derived from the initiator. As explained previously for diarylbutadienes (2), the adduct radicals Ph.COO.DPHX• and Ph.DPHX• (and the corresponding species containing units derived from DPOC) may engage in processes resembling primary radical termination; such reactions must occur by combination and not by disproportionation since an interaction of the latter type would leave initiator fragments in non-polymeric products and yet the presence of DPHX in the polymerizing system does not significantly affect the rate of entry into polymer of fragments derived from BPO.

The complexity of the NMR signals from the benzoate groups attached to DPHX or DPOC units (see Figure 2) indicates that, for units of both types, several structures are possible. In principle at least, DPHX and DPOC can give rise to 1,2-, 1,4- and 1,6- units and the latter to 1,8- units also; in each case, there can be stereoisomers. Clearly both DPOC and DPHX are very effective in capturing the benzoyloxy radical; they are respectively about 575 and not less than 243 times as reactive as MMA in that respect. These results for the polyenes conform to the view that any substance having an aryl group on the carbon atom to which the radical becomes attached and also extensive conjugation through its molecule is very reactive towards the benzoyloxy radical.

For a polymer of MMA prepared using BPO and DPOC, use can be made of the relationship

$$\frac{\text{no. of benzoate end-groups}}{\text{no. of phenyl end-groups}} = \frac{k_2[\text{MMA}]}{k_1} + \frac{k_2'[\text{DPOC}]}{k_1}$$

where k_1 is the rate constant for the decarboxylation of the benzoyloxy radical. The values of k_2/k_1 and k_2'/k_2 are taken as 0.31 mol^{-1} dm^3 and 575 respectively so that k_2'/k_1 is 178 mol^{-1} dm^3. Using the values of [MMA] and [DPOC] for the system giving the polymer referred to in Figure 2, it is deduced that the numbers of benzoate and phenyl end-groups in the polymer are almost equal and that 31% of the ester end-groups are attached to units derived from DPOC. This information can be used in connection with calculations concerning the number of benzoate end-groups and the sum of the numbers of aromatic and olefinic carbon atoms in the polymer.

In a comparison of the spectral area for the carbonyl carbons in benzoate end-groups with the area for aromatic and olefinic carbons, it must be noted that the carbonyl sites are enriched with carbon-13. For the polymer prepared in the presence of DPOC

$$\frac{\text{the total no. of aromatic and olefinic carbons}}{\text{no. of carbonyl carbons in benzoate end-groups}}$$

= (corrected ratio of spectral areas)x(enrichment factor for benzoate end-groups)

= 0.6 x 50 = 30

Aromatic and olefinic carbons are expected to occur at sites of several types viz. (a) benzoate end-groups, (b) phenyl end-groups, (c) the two phenyl groups in DPOC units adjacent to benzoate end-groups, (d) the six olefinic carbons in those DPOC units, (e) the phenyl and olefinic groups in DPOC units other than those adjacent to benzoate end-groups and (f) the unsaturated end-groups in units derived from MMA and formed as a result of disproportionation. The numbers of carbon atoms in various categories, for each carbonyl carbon in a benzoate end-group, are (a) 6, (b) 6, (c) 3.7 given by 2 x 6 x 0.31 and (d) 1.9 given by 6 x 0.31. If all interactions of polymer radicals occur by disproportionation, then the upper limit of the number of carbon atoms in category (f) is two i.e. 1/6th. of the sum of the numbers for categories (a) and (b). The sum of the numbers for all categories other than (e) is therefore not greater than 19.6. The difference between this number and the value of 30 estimated from the spectral data suggests that there is some incorporation of DPOC at sites other than those adjacent to benzoate end-groups; this conclusion is consistent with the view that some of the retardation caused by the presence of DPOC in the polymerizing system results from attack of growing polyMMA radicals on DPOC.

Similar conclusions can be reached from consideration of the polymer made in the presence of DPHX and referred to in Figure 2. If k_2'/k_2 is 243, the ratio of the numbers of benzoate and phenyl end-groups is 1:0.75 and 47% of the benzoate groups are adjacent to DPHX units. Following the procedure used in connection with DPOC, the numbers of carbon atoms in categories (a), (b), (c), (d) and (f) are respectively 6, 4.5, 5.6, 1.9 and 1.8 i.e. a total of 19.8. This number is to be compared with the estimate from spectral data, after allowing for enrichment and the Overhauser effect, of 50 aromatic or olefinic carbon atoms for each carbonyl carbon in benzoate end-groups.

The changes to DPHX on standing in toluene solution may be quite significant. The substance has been recommended (3) as a secondary solute for liquid scintillation counting, acting as a wavelength shifter emitting at wavelengths more suitable for photomultipliers of certain types. Structural changes in DPHX on storage in solution are indicated by the increase in molecular weight and by the decrease in power to retard polymerization; there must therefore be doubt about its suitability as a component of solutions to be used in scintillation counting. Similar uncertainty must arise in connection with its use as a rod-like fluorescent probe for study of lipid membranes (4). Mention was made (5) of fading of fluorescence after excitation; it was attributed to photo-isomerization from the all-trans form to a less fluorescent isomer but clearly changes of other types are also possible. Isomerization polymerization of conjugated polyenes, such as DPHX, has been reported as occurring quite readily to give complex products (6). DPOC undergoes Diels-Alder polymerization but it has been stated to be comparatively stable (7); this stability is consistent with the present finding that deterioration of solutions of DPOC is less marked than for solutions of the hexatriene.

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