Synthesis and reactions of a polyfunctional macroinitiator based on manganese carbonyl: uses in graft copolymerization

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The rapid reaction between polytetrafluoroethylene radicals and the benzene ring has been utilized in synthesizing a polyfunctional macroinitiator. For this purpose a copolymer of styrene and methyl methacrylate in acetic acid solution was allowed to react with polytetrafluoroethylene radicals generated photochemically from the monomer and manganese carbonyl. Analogy with the reactions of benzene, which have now been further studied, suggests that the radicals undergo both addition and substitution reactions with aromatic nuclei in the copolymer, so that the final copolymer carries grafts of short polytetrafluoroethylene chains with $Mn(CO)_5$ end-groups. At 100°C scission of CF_2—$Mn(CO)_5$ bonds occurs with formation of active radicals, so that the copolymer behaves as a polyfunctional macroinitiator. A study of the initiation mechanism is reported which shows that elimination of carbon monoxide precedes rupture of the CF_2—$Mn(CO)_5$ bond. Applications of the macroinitiators are exemplified by network formation on heating in styrene and graft polymerization with poly(*N*-vinyl-2-pyrrolidone). Reaction between poly(methyl methacrylate) and polytetrafluoroethylene radicals proceeds through hydrogen abstraction and radical recombination. It occurs less readily than interaction of the radicals with the copolymer, so that, for comparable conditions, the polytetrafluoroethylene grafts are longer and the product is less soluble.

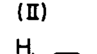
INTRODUCTION

It has been reported in an earlier paper[1] that the polymerization of tetrafluoroethylene in acetic acid solution is subject to powerful retardation by benzene, even when the latter is present in very low concentrations. The rate coefficient for reaction of the propagating radicals with benzene at 25°C has been estimated to be almost 50% greater than the propagation rate coefficient[1]. In the work referred to, photoinitiation of polymerization by manganese carbonyl was employed, so that the propagating radicals had the structure[2–5]:

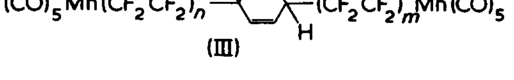
$$(CO)_5Mn(CF_2CF_2)_n^{\cdot}$$

(I)

We have studied further the interaction of these radicals with benzene and report below evidence consistent with the view that both substitution and addition reactions occur, leading to derivatives with structures typified by II and III:



(II)



(III)

Earlier work[6] has shown that the group $-CF_2CF_2Mn(CO)_5$ is unstable at temperatures in the region of 100°C, scission of C—Mn bonds occurring with generation of active free radicals. Therefore, as already reported[6], a polymer of structure IV:

$$\sim\sim\sim M \sim\sim\sim CF_2CF_2Mn(CO)_5$$

(IV)

(M being the repeating unit) is a macroinitiator which, on thermal decomposition in a polymerizable vinyl monomer, yields a block copolymer.

By utilizing the reactions outlined above we have generalized the concept of the macroinitiator to include polyfunctional macroinitiators. In the simplest example, synthesis of such a compound involves reacting radicals such as I with a preformed polymer containing benzene rings. This is described in the present paper, which is also concerned with some reactions of the new macroinitiators.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), tetrafluoroethylene, styrene (S), azobisisobutyronitrile (AIBN), manganese carbonyl, acetic acid (AR), and benzene (BDH Research Grade) were purified as described earlier[1,2,7,8]. AR methanol was used as supplied. Carbon monoxide (BOC Research Grade) was passed through a column cooled to −120°C in vacuum, condensed at −196°C and then fractionated.

The copolymer of styrene and methyl methacrylate was prepared by heating 80.6 ml MMA and 20.7 ml S with 2.40×10^{-2} mol l^{-1} AIBN at 60°C for 60 min, precipitat-

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ing in methanol, filtering and drying in a vacuum at room temperature. The yield was 7.13 g. The copolymer was twice reprecipitated in methanol from benzene solution to remove unreacted AIBN. The osmotic molecular weight of the copolymer was 148 000 and the calculated ratio of MMA to S units was 2.9:1 (reactivity ratios: MMA, 0.47; S, 0.50)[9].

Apparatus and techniques

All experiments were performed in a laboratory illuminated by inactive (sodium) light. The photochemical reactions were initiated by light of wavelength 435.8 nm, the optical system being essentially the same as that described earlier[2,10].

Techniques for determining the solubility of tetrafluoroethylene in acetic acid and benzene and for measuring the quantum input to reaction mixtures were similar to those already described[1,2,11]. The thermal reactions of the polyfunctional macroinitiator were studied gravimetrically at 100°C.

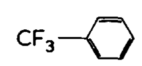
Manganese and fluorine contents of polymers were determined by neutron activation analysis carried out by the staff of the Universities Research Reactor (Risley). The molecular weights of the polymers were measured osmometrically.

U.v.–visible spectra were recorded with the aid of a Unicam SP800 spectrophotometer. Infra-red spectra of polymers, cast as films from chloroform on to a sodium chloride plate, were recorded by a Perkin–Elmer 577 spectrometer. Proton n.m.r. spectra were recorded using a Perkin–Elmer R12B 60 MHz spectrometer.

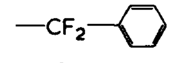
RESULTS AND DISCUSSION

Reactions of polytetrafluoroethylene radicals with benzene

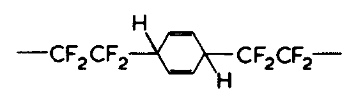
A solution of manganese carbonyl (40 mg) and tetrafluoroethylene (400 mg) in 1 ml benzene was irradiated with light of wavelength 435.8 nm. All volatiles were then removed by prolonged evacuation at room temperature; carbon tetrachloride was added to dissolve the residue and its n.m.r. spectrum was recorded. Two major peaks were found at $\tau = 2.5$ and 4.17, which we shall designate A and B, respectively. The spectrum of the monosubstituted benzene derivative



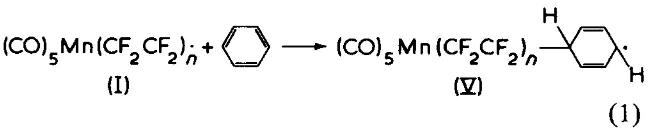
has a peak close to $\tau = 2.5$ (ref 12), so that in our system peak A probably arises from the structure



i.e. from II. We believe that peak B arises from a disubstituted cyclohexadiene structure e.g.

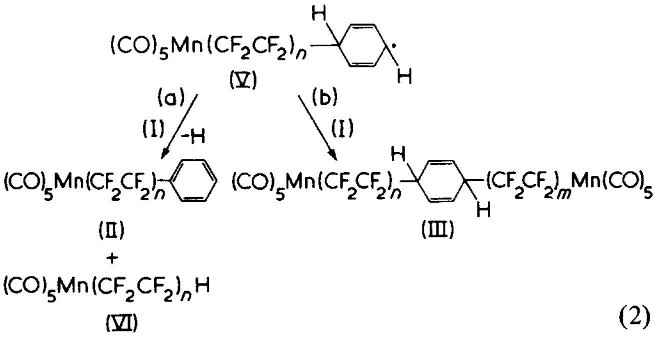


as present in III. Both types of product could be formed as a result of an initial addition reaction between the propagating radical (I) and benzene (equation 1):



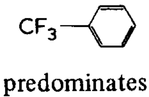
(1)

followed by hydrogen abstraction from the radical adduct (V) (equation 2a) or further addition to V (equation 2b):

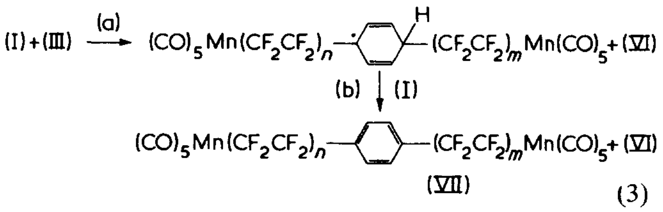


(2)

The corresponding products are II and III, respectively. This type of mechanism has been proposed by Charles and Whittle[13] in connection with the reaction of $\dot{C}F_3$ and benzene. However, in our system, the yield of III initially exceeds that of II whereas with $\dot{C}F_3$ formation of



(corresponding to II) predominates. If this difference is real, it may arise from shielding by the polymer chain of the H atom in V which is abstracted to give II. The relative intensities of peaks A and B are affected by the experimental conditions. The ratio of the integrated intensities B/A decreases with prolonged time of irradiation as shown in *Table 1*. We suggest this is due to hydrogen abstraction from III by the polytetrafluoroethylene radicals (I):



(3)

These processes would be expected to increase in importance as III accumulates, i.e. as the reaction time increases. Reaction (3b) would be expected to occur readily since it leads to rearomatization of the ring. Formation of the disubstituted benzene derivative (VII) is supported by the appearance of a shoulder in the n.m.r. spectrum at $\tau = 2.6$ on long irradiation. When the experiment is carried out in acetic acid solution with a low concentration of benzene (0.9 mol l^{-1}) smaller values of B/A are obtained (cf. *Table 1*); this result supports the above mechanism since at low [benzene] the radicals (I) are more likely to enter into the competitive reactions with III (equation 3a) with consequent reduction in B.

When a small quantity of bromine was added (in the

Table 1 Relative integrated intensities of peaks A and B. Reactions at 25°C

Time of irradiation (h)	B/A
1	1.53†
3	1.11†
200	0.49†
2	0.96*

* In acetic acid solution, [benzene] = 0.9 mol l^{-1}; † in bulk benzene

Table 2 Analytical data on polymers

Initial polymer, $\overline{M}_n$ after reaction	Mn content (ppm)	F content (ppm)	Mn atoms per chain	$\frac{[C_2F_4 \text{ units}]}{[\text{Mn atoms}]}$
Copolymer of MMA +S; 211 800	5210 ± 60	41 500 ± 3200	20.1	5.8
Poly(methyl methacrylate)				
Soluble fraction; 231 000	67 ± 2	1500 ± 200	0.28	16.3
Insoluble fraction	3180 ± 30	$(58.1 \pm 2.4)10^4$	–	132

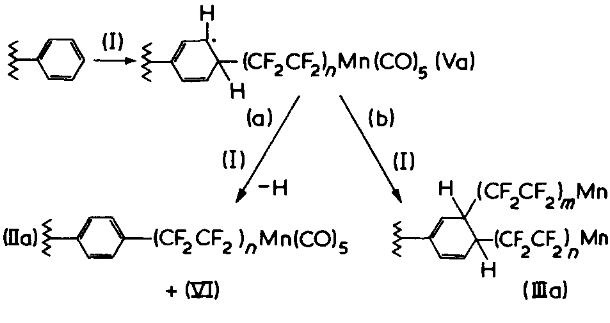
dark) to the products of irradiation (after removal of all volatiles) peak B steadily decreased, falling to about one-half of its original intensity in 0.5 h. The peak rapidly decayed when the mixture was irradiated by the light of a mercury arc. Peak A was not significantly affected during these experiments. Results of this type would be expected if peaks A and B are attributable to II and III, respectively.

According to the reactions set out above, formation of II and VII (equations 2a, 3a and 3b) is accompanied by the production of compound VI. The n.m.r. spectrum showed a shoulder at $\tau = 3.96$ which would be expected for this derivative[14,15]; two small peaks at $\tau = 3.11$ and 4.81 completed the expected triplet. When cyclohexane was used instead of benzene these peaks were seen more clearly, each being a triplet as would be anticipated.

Introduction of functional groups into a copolymer of methyl methacrylate and styrene

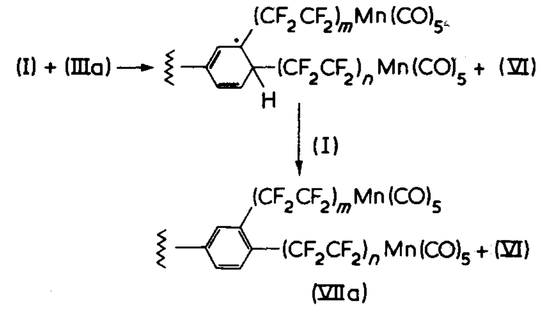
The reaction mixture consisted of 100 ml acetic acid containing $Mn_2(CO)_{10}$ (5.13×10^{-3} mol l^{-1}), C_2F_4 (0.14 mol l^{-1}) and 2 g of the copolymer of methyl methacrylate and styrene ($\overline{M}_n$ = 148 000) already described. It was irradiated (λ = 435.8 nm) for 5 h at 25°C, the incident intensity being 1.4×10^{-5} einstein l^{-1} s^{-1}. The copolymer was precipitated into methanol (2.5 l), filtered and washed five times with methanol and dried in vacuum at ambient temperature. The yield was 2.086 g. To ensure complete removal of free manganese carbonyl the polymer was re-precipitated from benzene solution into methanol four times; each benzene solution was filtered through a No. 4 sinter to remove any polytetrafluoroethylene. Finally the product was dried in vacuum at room temperature.

The data in *Table 2* show that the average copolymer chain carried 20.1 manganese atoms and 462.6 fluorine atoms or 115.6 C_2F_4 units. Thus each manganese atom is associated with an average of 5.8 C_2F_4 units, so that the average radical size before joining to the benzene ring was 5.8. By analogy with the results with benzene, we believe the reactions occurring are those shown below:



(4)

Similarly, during prolonged irradiation we might expect the process:



(5)

In equations (4b) and (5) we have assumed formation of *ortho* derivatives because positions in the ring near the polymer backbone would probably be somewhat shielded by the latter; however there is no direct experimental evidence for this assumption. It is important to note that the carbon radical intermediates in equations (4) and (5) are not reactive enough to initiate the polymerization of tetrafluoroethylene; this is indicated by the powerful retardation by benzene[1]. In addition to reactions shown there is also a small amount of crosslinking, evidenced by the increase in molecular weight of the copolymer. Since $20[Mn(CO)_5(C_2F_4)_{5.8}]$ became incorporated into each copolymer chain, the final expected molecular weight is 163 500 which is about 23% less than that observed. Crosslinking presumably occurs through combination of the carbon macroradicals referred to above.

The $Mn(CO)_5$ residues in the copolymer give rise to strong infra-red absorption bands near 2000 cm^{-1} (*Figure 1*) as expected on the basis of earlier results. The absorption in this region is very similar to that[16] of $CF_3Mn(CO)_5$ and $C_2F_5Mn(CO)_5$ and many examples of such absorption arising from terminal $-Mn(CO)_5$ groups in polymer chains are now known[1–5].

Initiation by polyfunctional macroinitiators

Figure 2 illustrates the polymerization of methyl methacrylate at 100°C in the presence of the polyfunctional initiator. In view of the low concentration of the latter (0.891 g l^{-1}) the initial rate (10^{-4} mol l^{-1}) is reasonably high. The rate of polymerization is decreased by carbon monoxide; for example, 650 torr of CO reduce the rate of initiation by a factor of 5.9 at 100°C (initiator concentration 0.045 g l^{-1}). It would seem therefore that the first step in radical formation is scission of CO, which is followed by rupture of

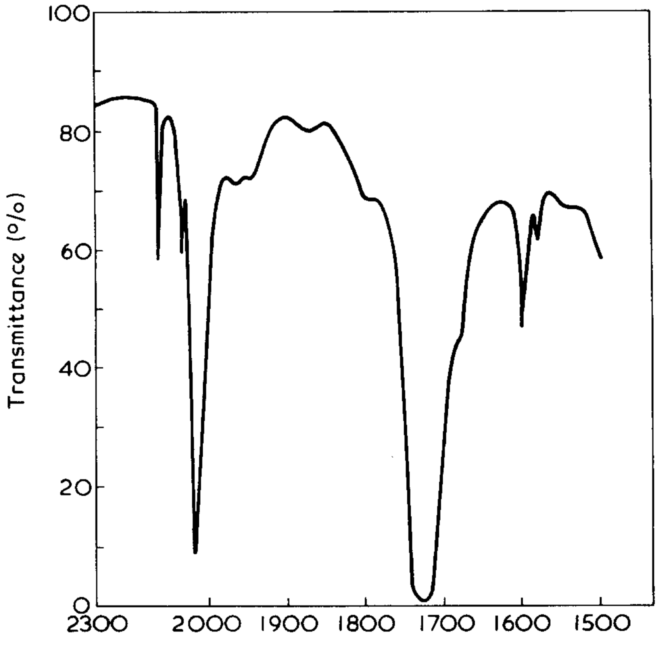


Figure 1 Infra-red spectrum of polyfunctional macroinitiator showing strong absorption of $-Mn(CO)_5$ near 2000 cm^{-1}. The absorptions at 1731 and 1603 cm^{-1} arise, respectively, from ester groups and aromatic rings in the copolymer

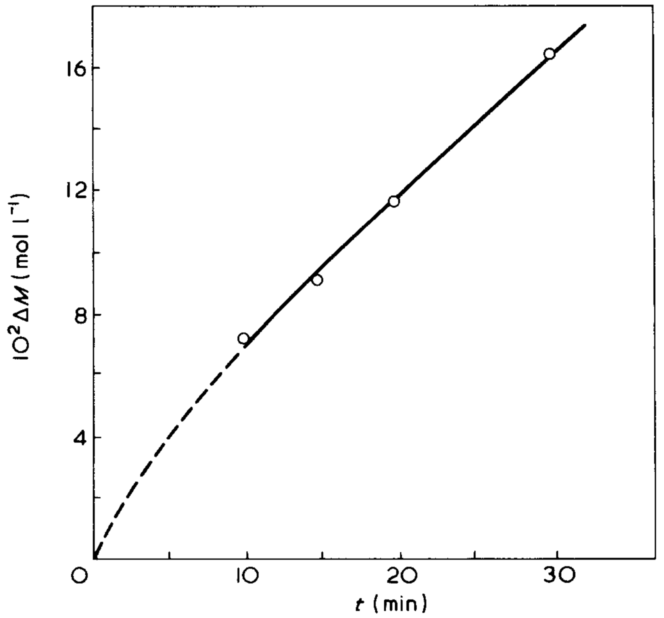
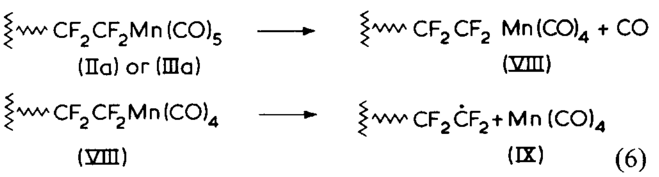


Figure 2 Polymerization of bulk methyl methacrylate at 100°C in the presence of polyfunctional macroinitiator, concentration 0.891 g l^{-1}

the C–Mn bond in the resultant species (VIII) to give the initiating macroradical (IX):



(6)

This mechanism is essentially similar to that deduced[17] for the low molecular weight model $CF_3Mn(CO)_5$.

In agreement with the radical-generating reactions shown in equation (6) we find that on heating the functionalized copolymer in benzene, acetic acid or styrene at 100°C, manganese carbonyl is formed, shown by the development of an absorption band having λ_{max} = 342 nm. Most probably $Mn_2(CO)_{10}$ arises from dimerization of $Mn(CO)_4$ followed by reaction with CO, or prior formation of $Mn(CO)_5$ and subsequent dimerization.

The dependence of rate of polymerization on initiator concentration is presented in *Figure 3*. Some retardation is apparent from the curvature of the rate –(concentration)$^{1/2}$ plot; this is consistent with similar findings[17] for the model compound $CF_3Mn(CO)_5$. *Figure 4* presents the rate of polymerization in the presence of carbon tetrachloride. In these experiments a low concentration of initiator (0.045 g l^{-1}) was used to minimize retardation. The rate of initiation (calculated from the conventional relation) corresponding to the plateau value is very close to twice that with $[CCl_4]$ = 0. Evidently the fragment $Mn(CO)_4$ formed in equation (6) generates a radical in the presence of CCl_4. A similar conclusion follows from *Figure 3*, although retardation obscures quantitative considerations.

Reactions of polytetrafluoroethylene radicals with poly (methyl methacrylate)

The reaction was carried out under conditions identical

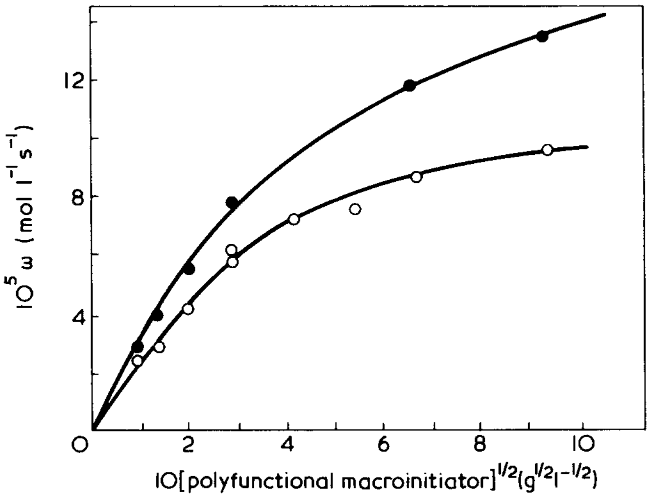


Figure 3 Dependence of rate of polymerization of bulk methyl methacrylate on [polyfunctional macroinitiator]$^{1/2}$ at 100°C. Mean rates over 15 min are plotted: ○, no additive; ●, 9.6 x 10^{-2} mol l^{-1} CCl_4

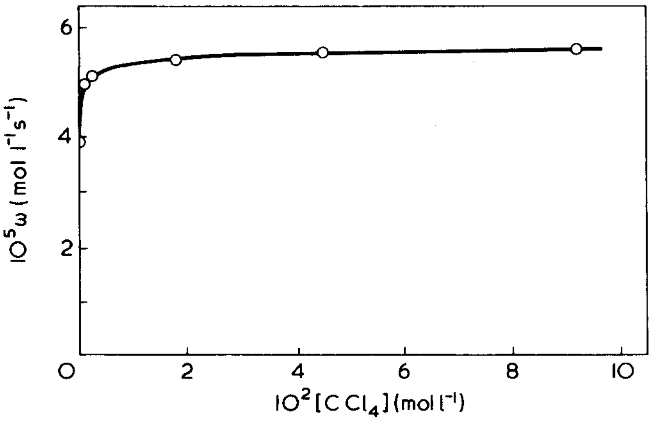
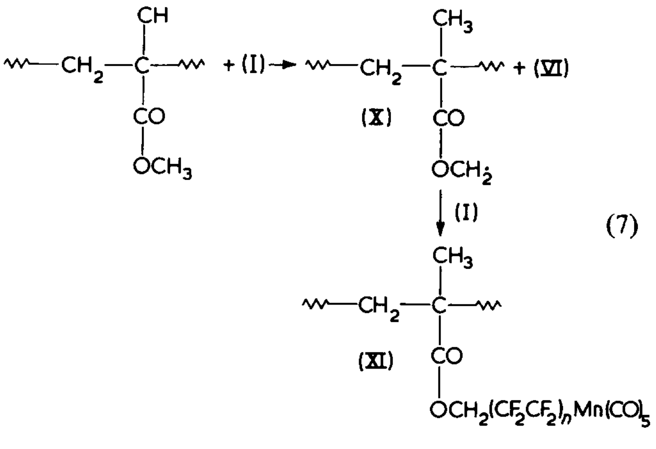


Figure 4 Dependence of mean rate of polymerization of bulk methyl methacrylate on $[CCl_4]$ at 100°C. Reaction time, 15 min; [polyfunctional macroinitiator] = 0.045 g l^{-1}

with those described for the methyl methacrylate–styrene copolymer, 2 g of poly(methyl methacrylate) ($\overline{M}_n$ = 215 000) being used. After a reaction time of 5 h the polymeric product was precipitated in methanol and dried. It weighed 2.91 g. The polymer was fractionated by extraction with benzene, the insoluble portion (1.09 g) being repeatedly washed and allowed to stand in a large excess of benzene for three days to remove unreacted manganese carbonyl. Both soluble and insoluble polymers were dried and analysed for Mn and F by neutron activation, with results presented in *Table 2*.

The incorporation of fluorine and manganese in the polymer in these experiments follows most simply from hydrogen abstraction from poly(methyl methacrylate) by polytetrafluoroethylene radicals and radical recombination to form structures such as XI:



(7)

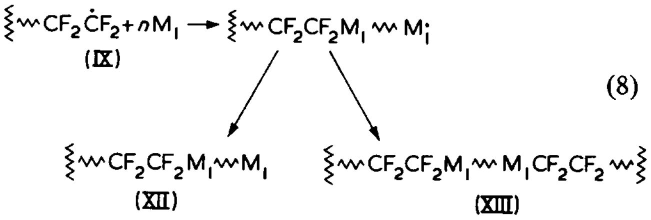
In our experience many aliphatic compounds (e.g. cyclohexane[1]) are strong retarders of the polymerization of C_2F_4 hence we think it unlikely that radical X is an effective initiator for C_2F_4 polymerization. These radicals (X) would therefore mainly combine with I as shown in equation (7), although a small proportion may interact to form crosslinks. Combination of I and radicals such as X provides the most likely mechanism for incorporating manganese into the polymer. This process would clearly be impeded by chain-transfer of I with solvent, so that these findings strongly support the view advanced earlier[1] that acetic acid is very inactive as a transfer agent in the polymerization of tetrafluoroethylene. In the present experiments the initial concentrations of acetic acid and poly (methyl methacrylate) were 17.5 mol l^{-1} and 0.2 base mol l^{-1}, respectively; these figures underline the difference in transfer activity of the two species.

According to *Table 2*, the increase in weight of the polymer attributable to the incorporation of $(CO)_5Mn(C_2F_4)_n$ units is 0.85 g, close to the observed value 0.91 g.

The ratio [C_2F_4 units incorporated] / [Mn atoms incorporated] is much greater when the initial polymer is poly (methyl methacrylate) than when it is the styrene–methyl methacrylate copolymer (*Table 2*). This implies that the latter is much more reactive than the homopolymer to the propagating radicals (I), so that the mean chain-length of the polytetrafluoroethylene units incorporated in the copolymer is smaller. Thus synthesis of a soluble product of high manganese content is greatly assisted by the presence of benzene rings in the initial polymer.

Applications of polyfunctional macroinitiators

The results described above show that radical generation by thermal decomposition of polyfunctional macroinitiators synthesized from the methyl methacrylate–styrene copolymer follows the route anticipated from the behaviour of monofunctional macroinitiators[6] and low molecular weight models[17]. In the presence of a vinyl monomer M_1 the product would be a graft polymer (XII) or a crosslinked polymer (XIII) (or both), depending on the mode of chain termination in M_1:



(8)

For example, a solution of 0.5 g of the macroinitiator in 10 ml styrene (at 25°C or 10.36 ml at 100°C) produced a gel on heating at 100°C for 67 min. We have also examined the graft copolymerization of *N*-vinyl-2-pyrrolidone. A solution of 50 mg macroinitiator in 5 ml (25°C) *N*-vinyl-2-pyrrolidone was degassed and heated to 100°C for 40 min. The resulting viscous solution was poured into petroleum ether (60°–80°) and the precipitated polymer was three times reprecipitated from methylene chloride into petroleum ether to remove unreacted monomer. The yield was 1.05 g, representing a 20-fold increase in weight over the original copolymer. Under identical conditions but without the polyfunctional macroinitiator only 3 mg of poly(*N*-vinyl-2-pyrrolidone) was formed. The solubility of the polymer in methylene chloride shows that the material is not extensively crosslinked. The graft copolymer is swollen but not dissolved by water and methanol.

These results encourage us to believe that the new polyfunctional macroinitiators may find applications in the synthesis of graft copolymers, particularly with hydrophilic/hydrophobic combinations.

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