Copolymerization of ω-Unsaturated Oligo(Methyl Methacrylate): New Macromonomers

P. Cacioli[a]; D. G. Hawthorne[a]; R. L. Laslett[ab]; E. Rizzardo[b]; D. H. Solomon[a]

[a] CSIRO Division of Applied Organic Chemistry, Melbourne, Victoria, Australia [b] Chemistry Department, Swinburne Institute of Technology, Hawthorn, Victoria, Australia

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P. CACIOLI, D. G. HAWTHORNE, R. L. LASLETT,*,†
E. RIZZARDO,* and D. H. SOLOMON

CSIRO Division of Applied Organic Chemistry
Melbourne, Victoria 3001, Australia

ABSTRACT

The free-radical copolymerization of ω-unsaturated oligo(methyl methacrylate) (1) with each of ethyl acrylate, styrene, methyl methacrylate, acrylonitrile, and vinyl acetate have been investigated. Incorporation of (1) into the polymer was observed in all cases although the molecular weights of the copolymers were substantially lower than those of the homopolymers obtained in the absence of (1) but under otherwise identical conditions. These experiments, together with a product study of the reactions of (1) with cyanoisopropyl radicals, have shown that the addition of free radicals to the double bond of (1) occurs readily. The sterically hindered radical so formed, however, undergoes facile β-scission, resulting in the termination of chains (chain transfer) in competition with chain propagation. The implications of these findings to the usefulness of (1) in the synthesis of graft copolymers and their relevance to the chemistry of free-radical polymerizations when methyl methacrylate is employed as a monomer or comonomer are discussed.

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*Authors to whom correspondence should be addressed.
†Visiting Scientist. Permanant address: Chemistry Department, Swinburne Institute of Technology, Hawthorn, Victoria 3122, Australia.

INTRODUCTION

An important termination mechanism in the free-radical polymerization of methyl methacrylate is disproportionation [1]. This gives rise to polymer chains of general formula (1) together with their saturated counterparts. Since the unsaturated molecules contain a potentially reactive double bond, the likelihood exists for their copolymerization with methyl methacrylate to give branched structures. This possibility appears not to have been seriously entertained before,

$$X \left(CH_2 - \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \right)_n CH_2 - C \underset{COOCH_3}{\overset{CH_2}{\diagup}}$$
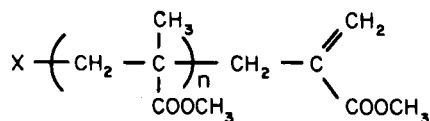
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and poly(methyl methacrylate) prepared by free-radical means is generally considered to be linear. Support for the possible involvement of (1) in copolymerization is expressed in the work of Bamford and White [2] who have observed the incorporation of poly(methyl methacrylate) into polyacrylonitrile when acrylonitrile was polymerized in the presence of poly(methyl methacrylate). This is rationalized most readily by invoking copolymerization of the unsaturated poly(methyl methacrylate) chains (1) with acrylonitrile. Further support is found in the work of Chikanishi and Tsuruta [3] who have shown that acrylates with bulky α-alkyl substituents can be copolymerized with suitable monomers, e.g., styrene.

Copolymerization of ω-unsaturated oligomers (macromonomers) with common monomers is of particular interest for the production of graft copolymers. Considerable worldwide interest [4] has been shown in macromonomers recently, and several of general formula (2), where R is a polymer chain, have been investigated. These are generally pre-

$$CH_2 = \underset{\underset{COOR}{|}}{\overset{\overset{CH_3}{|}}{C}}$$
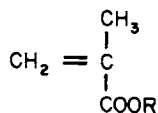
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pared by a two-step synthesis involving both functional initiators and functional chain-transfer agents followed by conversion of the end group to a methacryloyl unit. No reports have appeared on the copolymerization behavior of the more readily accessible ω-unsaturated

oligomers of type (1). These (X = H) have recently become available in high purity by the use of cobalt porphyrins [5] or cobaloximes [6] as catalytic chain transfer agents in the polymerization of methyl methacrylate. In addition, the potentially more useful oligomers (1) in which the end group (X) can include functional substituents can now be obtained by using suitable alkoxyamines as initiators-terminators for the free-radical polymerization of methyl methacrylate [7].

This paper reports on the free-radical copolymerization of ω-unsaturated oligo(methyl methacrylate) (1) with ethyl acrylate, styrene, methyl methacrylate, acrylonitrile, and vinyl acetate, as well as the chemistry involved in the attempted homopolymerization of (1). Mention is also made of preliminary copolymerization experiments with ω-unsaturated oligomethacrylonitrile.

EXPERIMENTAL

Materials

All monomers were purified by conventional methods, stored at -10°C, and redistilled immediately before use. ω-Unsaturated oligo-(methyl methacrylate)s of various number-average molecular weights were prepared by the oligomerization of methyl methacrylate (15 g) in ethyl acetate (60 mL) at 60°C for 48 h, using methyl azoisobutyrate (100 mg) as the initiator and Co^{II} tetraphenylporphyrin (2-12 mg) as the catalytic chain-transfer agent [5]. The reactions were performed in sealed glass vessels after degassing the solutions by four successive freeze-pump-thaw cycles to 10^{-3} torr. The oligomers were freed from catalyst by filtration through Kieselgel 60 in ethyl acetate solution and could be fractionated by careful chromatography on the same adsorbent using mixtures of 2-10% ethyl acetate in benzene as eluent. Pure dimer and trimer were obtained in this way or by distillation on a Kugelrohr apparatus (dimer, bp 110°C/0.2 torr; trimer, bp 150°C/0.2 torr). The ^{1}H-NMR of the ω-unsaturated oligo(methyl methacrylate) exhibited signals at δ 6.2 and 5.5 (olefinic CH_2), 3.6 (OCH_3), 2.5 (allylic CH_2), 1.9 (backbone CH_2), and 1.0 (CH_3).

ω-Unsaturated oligomethacrylonitrile was prepared in a similar fashion. ^{1}H-NMR of dimer: δ6.1 and 5.9 (olefinic CH_2), 2.5 (allylic CH_2), 1.5 (CH_3), ^{1}H-NMR oligomers: δ6.2, 6.0, 2.5, 1.5.

Procedures

Copolymerizations were carried out in sealed glass tubes on degassed solutions of monomer (10 mmol), macromonomer (see Table 1), and azobisisobutyronitrile (7 mg) in benzene (2 mL) at 60°C for

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TABLE 1. Copolymerization of Oligo(Methyl Methacrylate) Macromonomers (1) with Various Monomers[a]

Monomer	Experiment	Macromonomer $\overline{M}_n$	Macromonomer in feed, mol%	Conversion,[b] %	Product, $\overline{M}_n$	Macromonomer in product, mol%
Ethyl acrylate	A	-	-	95	270 000	-
	B	680	5.9	91	41 000	5.8
	C	1 000	12.0	95	36 000	11.0
Styrene	D	-	-	92	21 000	-
	E	540	7.7	51	4 800	5.3
	F	200	8.3	45	8 200	8.9
Methyl methacrylate	G	-	-	99	26 000	-
	H	680	5.9	71	9 300[c]	1.7
Acrylonitrile	I	-	-	100	d	
	J	680	5.9	53	d	1.5
Vinyl acetate	K	-	-	87	20 000	-
	L	680	5.9	-	1 100[e]	38
	M[f]	200	8.0	-	840	53
	N	200	8.0	-	950	44

[a]10 mmol monomer, 2 mL benzene, 7 mg AIBN, 60°C, 7 days.
[b]Weight of polymer as a percentage of the total macromonomer plus monomer in the feed.
[c]After chromatography, macromonomer-free fractions combined.
[d]The MW of the polymer was not determined because of its poor solubility in solvents suitable for GPC analysis.
[e]Includes unreacted macromonomer.
[f]In this experiment, 20 mg AIBN was used.

7 days. Various techniques were then employed to isolate and purify the products (vide infra).

The oligomers chosen for study were generally of low MW ($\overline{M}_n \approx$ 1000) so that their incorporation into polymer chains could be more readily followed by monitoring the disappearance of their olefinic protons by ^{1}H spectroscopy. A low (< 0.12) mole ratio of macromonomer to monomer was used in the copolymerizations, and these were carried to high conversion to minimize the amount of unreacted macromonomer. A slow rate of initiation was used to maximize the MW of graft copolymer. This facilitated the removal of any unreacted macromonomers which, because of their low MW, were soluble in solvents such as petroleum spirit and methanol.
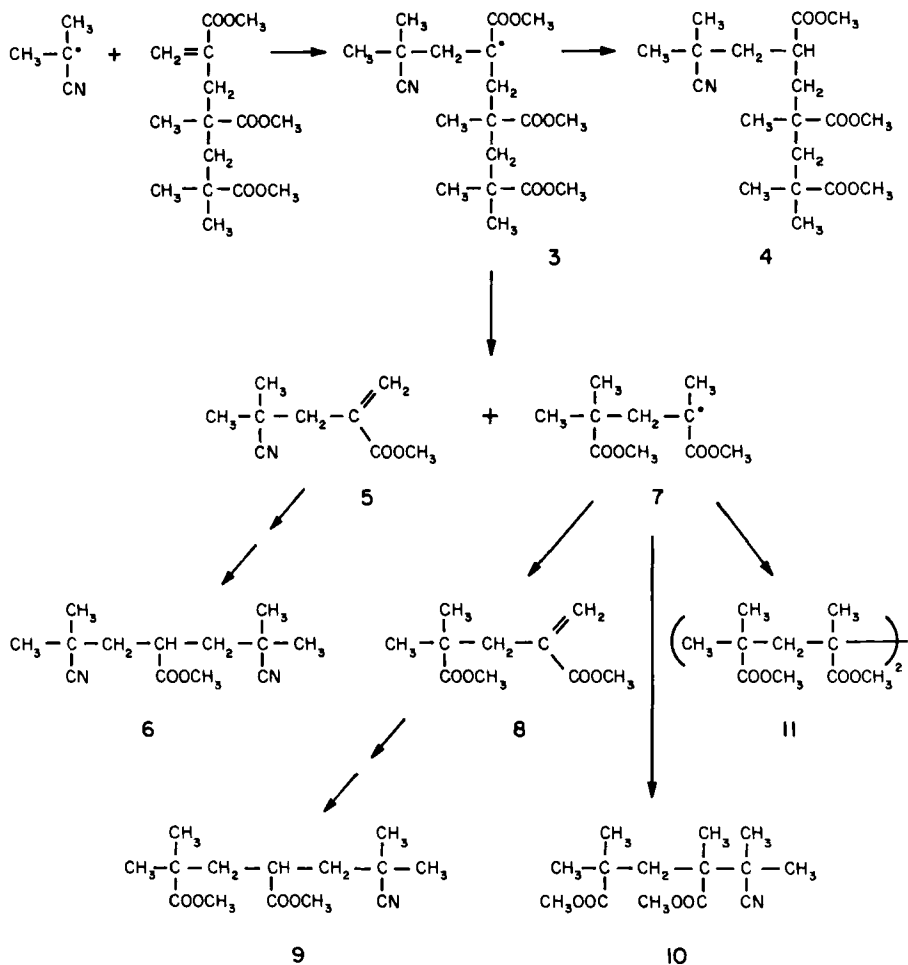
The degree of grafting of the macromonomer was evaluated by ^{1}H-NMR spectroscopy of the purified products. The ratio of the integrals for the methoxy signals of the macromonomers to the integrals for appropriate protons of the backbone polymer was used to estimate the extent of macromonomer incorporation. GPC was used as a guide for number- and weight-average molecular weights although it is realized that GPC does not provide accurate values for branched polymers.

^{1}H-NMR spectra were recorded on a Varian EM390 spectrometer using $CDCl_3$ as solvent and $SiMe_4$ as internal standard, unless otherwise stated. GPC analyses were performed on a Waters Associates instrument equipped with differential refractometer and μ-Styrogel columns of 10^6, 10^5, 10^4, 10^3, and 500 Å. Tetrahydrofuran solvent was used at a flow rate of 1 mL/min. Results were derived from polystyrene standards by using the Chromatix-1 GPC program. HPLC analysis and separations were carried out by using a Du Pont 850 chromatograph equipped with a variable wavelength detector, LDC 308 computing integrator, 25 cm $\times$ 10 mm Ultrasphere ODS column and employing acetonitrile/tetrahydrofuran mixtures as the eluting solvents. Light-scattering studies were performed on a Chromatix KMX-6 photometer using tetrahydrofuran as solvent. GLC-mass spectral determinations were performed on a Finnigan 3300 mass spectrometer using a 3% Dexil 300 GLC column and methane as the reagent gas for chemical ionization.

RESULTS AND DISCUSSION

Homopolymerization

Attempted polymerization of macromonomer (1) in benzene with 7 mol% azobisisobutyronitrile as initiator at 60°C resulted in little change. The NMR of the product was essentially the same as that of the starting macromonomers, with no more than a 10% decrease in the relative intensity of the signals for the olefinic protons. GPC revealed no significant increase in molecular weight.

$$CH_3-\overset{\underset{\displaystyle CN}{|}}{\underset{}{\overset{\displaystyle CH_3}{|}}}C^{\cdot} \;+\; CH_2=\overset{\displaystyle COOCH_3}{\underset{}{C}} \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-CH_2-\overset{\displaystyle COOCH_3}{C^{\cdot}} \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-CH_2-\overset{\displaystyle COOCH_3}{CH}$$

3   **4**

5   **7**

6   **8**   **11**

9   **10**

SCHEME 1.

In order to determine whether or not the cyanoisopropyl radical was capable of addition to the double bond of (1) and, if so, to examine the fate of the radical so formed, 0.55 mol equivalents of AIBN was reacted with pure trimer (1) (X = H, n = 2) in benzene at 60°C for 160 h. The resulting mixture of products was separated by gas chromatography and the molecular weight of each component was determined by mass spectrometry. These data, together with ^{1}H-NMR analysis of the crude mixture, showed that approximately 70% of the trimer (1) had been consumed and also allowed structures to be assigned to most of the prod-

ucts. Those assigned structures (4), (5), (6), (8), (9), (10), and (11) (Scheme 1) account for over 90% of the trimer consumed, and all can be seen to derive from macroradical (3) formed by the addition of cyanoisopropyl radical to trimer (1). Hydrogen abstraction by radical (3) would give (4), m/e 369. This product is obtained in low yield (<5%), while an even more minor constituent (<1%), detected with m/e 367, could arise by loss of a hydrogen atom from (3). Interestingly, (5), (6), (8), and (9) or (10) were the major products of the reaction. The formation of these compounds can be explained by the macroradical (3) undergoing β-scission to give, initially, product (5), m/e 167, and radical (7).

It should be noted that the alternative, and perhaps equally favored, mode of β-scission of radical (3) would give the starting reactants. On this basis, the addition of cyanoisopropyl radical to macromonomers (1) is likely to be reversible.

The structure assigned to product (5) (also isolated in these laboratories from a different source) was supported further by the presence of its characteristic olefinic resonances in the ^{1}H-NMR (δ5.9 and 6.5) of the crude reaction mixture and by the formation of products of the reaction of (5) with cyanoisopropyl radicals, namely (6), m/e 236, and its related olefin, m/e 234.

The other product of the β-scission of (3), radical (7), may disproportionate to give the olefin (8), m/e 200, combine with itself to give (11), m/e 402, or combine with a cyanoisopropyl radical to form (10), m/e 269. An isomer of (10), compound (9), could be formed by addition of cyanoisopropyl to olefin (8) followed by the resulting radical abstracting a hydrogen atom. Thus, the peak with m/e 269 could be due to either (9) or (10) or a mixture of both.

With regard to the use of ω-unsaturated oligo(methyl methacrylate) as macromonomer in copolymerizations, it is pertinent to note that highly sterically crowded radicals such as (3) appear not to undergo self-combination nor combination with somewhat less crowded radicals, such as the cyanoisopropyl. GLC analysis of the above reaction mixture, using conditions which would have resolved oligomers up to octamer, revealed the absence of the product from the self-combination of radical (3). The products of highest MW were pentameric compounds with m/e 469 and 502 (formed in trace amounts), and there was no indication of a product with m/e 436 which would have resulted by combination of radical (3) with cyanoisopropyl.

In summary, the above experiment demonstrates that radical addition to the double bond of ω-unsaturated oligo(methyl methacrylate) occurs readily and that the resulting radical (of type (3)) undergoes mainly β-scission in the absence of reactive substrates. Furthermore, radical (3) shows little tendency to undergo combination reactions while disproportionation processes are of minor importance.
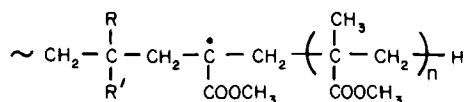
Copolymerizations

(a) Copolymerization of (1) and of Oligomethacrylonitrile with Ethyl Acrylate

Copolymerization of (1) [(a) $\overline{M}_n$ 680; (b) $\overline{M}_n$ 1 000] with ethyl acrylate under the standard conditions described above gave rise to a high yield of graft copolymer (Experiments B and C, Table 1). GPC analysis showed no unchanged macromonomer in the product from Experiment B and barely a trace was detected in that from Experiment C. The NMR spectra of the unpurified copolymers showed no olefinic protons in either sample, and the molar ratio of macromonomer (δ3.6, OCH_3) to ethyl acrylate (δ4.1, OCH_2) was approximately equal to that in the feed. Examination of the mother liquors after precipitation of the product of Experiment B from petroleum spirit (bp 40-60°C) also failed to reveal any unchanged macromonomer.
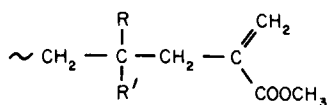
These results, using the GPC-derived molecular weight (see Table 1), indicate the incorporation of at least 12 macromonomer units per chain. Thus the behavior of (1) compares favorably with the macromonomer of formula (2) which Yamashita [8] copolymerized with perfluoroalkyl acrylate.

The branched structure for our graft copolymer is supported further by MW studies. Light-scattering measurements of the product from Experiment C gave $\overline{M}_w$ 85 000, whereas the $\overline{M}_w$ by polystyrene-calibrated GPC was 56 000. When a linear poly(ethyl acrylate) was examined by these techniques, the two values obtained were in good agreement (within 10%). Surprisingly, Yamashita [9] found membrane osmometry to give results similar to polystyrene-calibrated GPC for the MW determination of poly(perfluoroalkyl acrylate) with 4 to 8 poly(methyl methacrylate) branches ($\overline{M}_n$ 3 000) per chain.

As can be seen from Table 1, the molecular weight of the graft copolymer in Experiments B and C ($\overline{M}_n$ 41 000 and 36 000, respectively) is substantially lower than that of the poly(ethyl acrylate) ($\overline{M}_n$ 270 000) produced in the absence of macromonomer but under otherwise identical conditions (Experiment A). This is most likely a result of the low reactivity of the highly hindered radical (12, R = H, R' = $COOCH_2CH_3$), formed by incorporation of macromonomer, toward ethyl acrylate. This low rate of addition (propagation) would increase the opportunity for radical (12) to undergo chain transfer via β-scission or termination by disproportionation (see attempted homopolymerization of (1) and Scheme 1). Although combination of radicals of type (12) with the cyanoisopropyl radical is not competitive with β-scission (see Scheme 1), combination of type (12) radicals with the less-hindered polyacrylyl radicals may occur.

$$\sim CH_2 - \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}} - CH_2 - \overset{\displaystyle \bullet}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}} - CH_2 - \left(\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}} - CH_2 \right)_{\!n} H$$
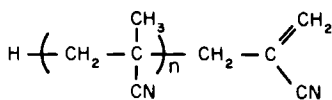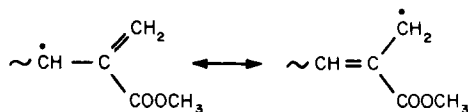
12

$$\sim CH_2 - \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}} - CH_2 - C \overset{\displaystyle \nearrow CH_2}{\underset{\displaystyle \searrow COOCH_3}{}}$$

13

$$H \left(CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}} \right)_{\!n-1} CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}{}^{\bullet}$$

14

$$H \left(CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}} \right)_{\!n} CH_2 - C \overset{\displaystyle \nearrow CH_2}{\underset{\displaystyle \searrow CN}{}}$$

15

$$\sim \overset{\displaystyle \bullet}{C}H - C \overset{\displaystyle \nearrow CH_2}{\underset{\displaystyle \searrow COOCH_3}{}} \longleftrightarrow \sim CH = C \overset{\displaystyle \nearrow \overset{\bullet}{C}H_2}{\underset{\displaystyle \searrow COOCH_3}{}}$$
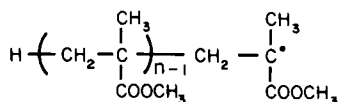
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The olefins resulting from β-scission would have structure (13) (R = H, R' = $COOCH_2CH_3$) and could also act as macromonomers.

Hence, it is probable that the final product contains both poly(methyl methacrylate) and poly(ethyl acrylate) branches. Furthermore, the radical product (14) of the β-scission process would initiate new chains, resulting in the formation of poly(methyl methacrylate) sequences as chain ends in the poly(ethyl acrylate) backbone.

An added possibility for chain termination is that of chain transfer to macromonomer (1) by way of the propagating radical (12) abstracting an allylic hydrogen from (1). This pathway has not been detected in this copolymerization but appears to be a significant process in the copolymerization of macromonomer (1) with vinyl acetate (see below).

Preliminary copolymerization experiments with ω-unsaturated oligomethacrylonitrile of general formula (15) and ethyl acrylate (molar ratio 0.07:1) indicate a somewhat lower extent of incorporation of (15) compared to macromonomer (1) (these results were obtained in more dilute solutions than the normal runs due to the lower solubility of (15) in benzene). GPC measurements showed unreacted

macromonomer (15) as well as polymer of $\overline{M}_n$ 7 500 presumed to be poly(ethyl acrylate-g-methacrylonitrile). This presumption was supported by the ^{1}H-NMR spectra, which showed an approximate 25% reduced intensity for the olefinic protons due to macromonomer ($\delta 6.2$) as well as the characteristic signals due to polymeric ethyl acrylate (e.g., $\delta 4.1$, OCH_2).

(b) Copolymerization of (1) with Styrene

The copolymerization of (1) ($\overline{M}_n$ 540) with styrene (Experiment E, Table 1) resulted in a lower yield of less-branched copolymer compared with ethyl acrylate (Experiment B) under the same conditions. Unreacted macromonomer was detected by both GPC and NMR analyses and largely removed by precipitation of the polymer from methanol. The NMR spectrum of the purified copolymer ($\overline{M}_n$ 4 800) showed no olefinic protons and a mole ratio of macromonomer ($\delta 2.7$-3.7, OCH_3) to styrene ($\delta 6.2$-7.4, ArH) of 1:18. The broadening of the methoxyl signal in the copolymer compared to that in the macromonomer ($\delta 3.6$) provides further evidence for the poly(styrene-g-methyl methacrylate) structure since studies [10] with styrene-methyl methacrylate copolymers have demonstrated how the NMR signals of the methoxyl groups in such copolymers are affected by nearby phenyl rings.

To remove any last trace of unreacted macromonomer and determine whether styrene homopolymer was produced along with the copolymer, the methanol-precipitated product was examined by reverse-phase high-performance liquid chromatography (HPLC). The first fraction contained a trace of macromonomer. The main peak corresponding to poly(styrene-g-methyl methacrylate) was divided into two separate fractions, found to have $\overline{M}_n$ of 4 400 and 9 700. These were shown to be entirely free of unreacted macromonomer by further HPLC analysis. Under the HPLC conditions used, any homopolymer of styrene would be expected to be the material of longest retention time. However, NMR analysis indicated the presence of approximately two macromonomer units per chain in both fractions.

In this copolymerization a significant decrease in the molecular weight of the copolymer ($\overline{M}_n$ 4 800, Experiment E, Table 1) compared to the control ($\overline{M}_n$ 21 000, Experiment D) was again noted.

Chain transfer via β-scission (see Scheme 1) of the macromonomer-derived radical (12, R = H, R' = Ph) is again likely to be a significant process involved in the reduction of molecular weight, but it should be noted that this process alone would result in the introduction of less than one macromonomer per polymer chain. Hence it can be concluded that normal copolymerization of (1) with styrene is taking place.

A search of the NMR spectra of the crude product for olefins of structure (13, R = H, R' = Ph), which would be formed in the β-scission of (12, R = H, R' = Ph), was inconclusive. It should be noted, however, that a considerable proportion of macromonomers (13), if formed, could be incorporated into the polymer.

Because the macromonomer used in the above experiment is likely to contain dimer (1, X = H, n = 1) and since it could be argued that the less-hindered double bond of the dimer might be more reactive toward addition, the possibility of its preferential incorporation was investigated by examining the copolymerization of pure dimer with styrene (Experiment F, Table 1). The dimer does in fact appear to be incorporated more efficiently and the polymer formed is of higher MW. Surprisingly, however, a corresponding increase in yield was not observed (compare Experiments F and E).

(c) Copolymerization of (1) with Methyl Methacrylate

Copolymerization experiments with macromonomer (1) and methyl methacrylate are of particular interest since they could show whether or not the unsaturated chains formed in the homopolymerization of methyl methacrylate can copolymerize with methyl methacrylate to give branched polymers.

Copolymerization of macromonomer (1), ($\overline{M}_n$ 680) with methyl methacrylate resulted in some incorporation of (1) (Experiment H). Careful analysis of the product by ^{1}H-NMR showed that approximately 25% of the macromonomer had been consumed, based on the reduction in the intensity of the olefinic protons. The crude mixture was chromatographed on Sephadex LH20 and the high molecular weight fraction ($\overline{M}_n$ 9 300) was shown to be devoid of unchanged macromonomer by GPC analysis. If we assume that the 25% of macromonomer consumed is all incorporated in this polymer, then there would be approximately 2 macromonomer units per chain. It should be noted, however, that if β-scission of the macromonomer-derived radical (12, R = CH_3, R' = $COOCH_3$) is occurring, and this is most likely (see Scheme 1), new olefins of structure (13, R = CH_3, R' = $COOCH_3$) would be formed, and the estimation of branching, based on the amount of olefin consumed, would be conservative.

Clearly, the detection of copolymerized macromonomer is rendered more difficult in this case by the fact that both the backbone and the macromonomer have the same chemical composition.

Attempts to establish the existence of branching by molecular weight studies using GPC, light scattering, and osmometry proved inconclusive, due, we believe, to the insensitivity of these techniques for the detection of a low concentration of short branches. Nevertheless, that macromonomer is consumed and that its presence induces chain termination (lowering of MW) demonstrates that the ω-unsaturated poly(methyl methacrylate) formed during homopolymerization

of methyl methacrylate is subject to further reactions in the polymerizing medium. These reactions would have important implications in relation to both the structure and the kinetics of formation of the final polymer, especially for polymerizations carried out to high conversion. For example, the number of unsaturated end groups in the polymer would be lower than that predicted from a knowledge of the termination mechanism, while the chain transfer to polymer observed during free-radical polymerization of methyl methacrylate may be explained in part by the β-scission of the macromonomer-derived radical (12, R = CH_3, R' = $COOCH_3$). Because of this importance, further information about the degree and mode of incorporation of these macromonomers into poly(methyl methacrylate) is now being sought in our laboratories.

(d) Copolymerization of (1) with Acrylonitrile

Copolymerization of acrylonitrile with 5.9 mol% of the unsaturated methyl methacrylate oligomer (1) ($\overline{M}_n$ 680) gave a yellowish solid in reasonable yield (Experiment J). Filtration allowed easy separation since macromonomer (1) is benzene soluble. ^{1}H-NMR spectra (in d_6-DMSO) of the purified product indicated the absence of unreacted macromonomer and 1.5 mol% of incorporated macromonomer ($\delta 3.5$, OCH_3 versus $\delta 3.1$, CH of polyacrylonitrile).

This rather low extent of incorporation is surprising in view of the results with ethyl acrylate (Experiments B and C) and the fact that the reactivity ratios for acrylonitrile and ethyl acrylate with methacrylate monomers are similar [10]. The answer may lie in the insolubility of the copolymer in the polymerization medium (benzene). Under these conditions, propagation is governed by the rate of diffusion of monomer to the propagating radical, which could be slow for the relatively large macromonomer. Hence, increased preference for incorporation of the more mobile acrylonitrile monomer could result.

(e) Copolymerization of (1) with Vinyl Acetate

The attempted copolymerization of (1) ($\overline{M}_n$ 680) with vinyl acetate resulted in the formation of only low-MW material ($\overline{M}_n$ 1 100, including unreacted macromonomer, Experiment L). Because of foreseen experimental difficulties, no attempt was made to isolate the product (formed in low yield), but inspection of the ^{1}H-NMR spectrum indicated that the resultant copolymer consisted of approximately 38% (1) on a molar basis.

Copolymerization of the methyl methacrylate dimer (1, X = H, n = 1) with vinyl acetate gave comparable results (Experiment M). In this case the unreacted dimer could be removed easily and completely by distillation (120°C, 0.005 torr) leaving a small yield of copolymer with $\overline{M}_n$ = 840 and comprising approximately 53% incorporated dimer

on a molar basis. These results indicate that macromonomers (1) can enter into propagation reactions during the polymerization of vinyl acetate, but termination reactions clearly predominate. This is perhaps not surprising if one considers, as a guide, the reactivity ratios of MMA (M_1) and VA (M_2) ($r_1 \approx 20$, $r_2 \approx 0.02$) [11]. Thus, while the addition of the vinyl acetate propagating radical to macromonomer (1) is likely to occur readily, the radical (12, R = H, R' = OAc) so formed would have very little tendency to add either to macromonomer or vinyl acetate.

The ^{1}H-NMR spectrum of the copolymer from dimer (1, X = H, n = 1) and vinyl acetate exhibited weak resonances from olefinic protons at the same chemical shift as those from dimer (1) ($\delta 6.2$ and 5.5) but not the corresponding and more intense resonance from the allylic hydrogens ($\delta 2.6$) of (1). This suggests reaction at the allylic position and may reflect the relatively high propensity for hydrogen abstraction by the vinyl acetate propagating radical [12]. Abstraction of allylic hydrogens from (1) would constitute a further plausible mechanism for chain termination (chain transfer). However, in order to preserve the characteristic olefinic resonances from (1), the allylic radical (16) would need to react exclusively at the more-hindered secondary position and even this would generally be expected to perturb the resonances of the vinylic hydrogens to a measurable extent. The alternative possibility in which the olefins (E and Z) formed by reaction of (16) at the primary position give rise to ^{1}H resonances in the olefinic region similar to those from (1) is also difficult to rationalize. This observation, therefore, remains unexplained.

CONCLUSIONS

The experiments described here demonstrate that the double bond of ω-unsaturated poly(methyl methacrylate) (1), although hindered, is not inert to attack by free radicals. In fact, addition of free radicals to this olefin appears to be a remarkably facile process as even the tertiary cyanoisopropyl radical undergoes addition with surprising efficiency (see attempted homopolymerization of 1). The limitations in the use of ω-unsaturated oligo(methyl methacrylate) as macromonomers for the synthesis of graft copolymers, stem from the low reactivity of the macromonomer derived radical (12) toward double bond addition and the fact that the facile β-scission of (12) results in chain transfer which reduces substantially the MW of the polymers.

In spite of these limitations, however, we have found that useful incorporations of (1) can be obtained in its copolymerizations with various monomers (see Table 1). In particular, copolymerizations of (1) with ethyl acrylate (and presumably other alkyl acrylates) or styrene give rise to copolymers with compositions approaching very closely those of the initial monomer feed. Macromonomer (1) reacts most

readily with the vinyl acetate propagating radical although subsequent chain terminating reactions give rise to only low MW copolymer, while an intermediate efficiency in the incorporation of (1) is observed with methyl methacrylate or acrylonitrile as comonomers.

The reactions of macromonomer (1) outlined above have significant implications, in relation to the structure of the polymers and the kinetics of their formation, for polymerizations in which methacrylates (or methacrylonitrile) are used as monomers or comonomers since during these polymerizations ω-unsaturated chains of the type investigated in this study are generally formed by disproportionation of the propagating radicals.

ACKNOWLEDGMENTS

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