

NMR STUDIES OF FREE-RADICAL POLYMERIZATION AND COPOLYMERIZATION OF MONOMERS AND POLYMERS CONTAINING ALLYL GROUPS

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Abstract—Reactivity ratios for free-radical copolymerization of allyl acetate (A) with (i) methyl methacrylate (M), (ii) n-butyl acrylate (B) and (iii) styrene (S) have been evaluated from either copolymer compositions or dyad fractions determined by ¹H and ¹³C-NMR spectroscopy; the values obtained are respectively: (i) $r_A = 0.024 \pm 0.009$ and $r_M = 41 \pm 6$, (ii) $r_A = 0.04 \pm 0.02$ and $r_B = 11.7 \pm 1.0$, and (iii) $r_A = 0.021 \pm 0.001$ and $r_S = 66 \pm 4$. These values indicate that in copolymerizations of allyl methacrylate with (meth)acrylates and styrene, conversion of the allylic C=C bonds will only become significant when the extent of reaction of all other types of C=C bonds has reached very high values. NMR studies of the structure of poly(allyl methacrylate) formed by both bulk and dilute solution polymerization have provided no evidence for the in-chain lactone rings which may result from intramolecular cyclopolymerization of allyl methacrylate; the signals in the NMR spectra of poly(allyl methacrylate) are entirely consistent with “normal” polymerization at the methacrylic and allylic C=C bonds. Theoretical predictions based upon the measured reactivity ratios, and results from a model reaction, indicate that the very low concentrations of pendant methacrylic C=C bonds which result from polymerization of the allylic C=C bonds in molecules of allyl methacrylate, make a significant contribution to grafting and crosslinking.

INTRODUCTION

Free-radical homopolymerizations of allylic monomers, which have the general structure $\text{CH}_2=\text{CR}-\text{CH}_2-\text{X}$, are well known to proceed at low rates and to yield polymers of low molar mass. This is commonly believed to be due to “autoinhibition” arising from hydrogen atom abstraction from the allylic methylene group (i.e. chain transfer to monomer, which is facile compared to addition to the C=C bond), followed by loss of the resulting allylic radicals via radical coupling reactions [1–4]. ESR experiments have shown that although allylic radicals are formed in polymerization of allylic monomers, they are only present at low concentration [5]. Autoinhibition limits the achievable degrees of polymerization to values below 20 and prevents the preparation of useful linear homopolymers from allylic monomers. In spite of this restriction, monomers containing allylic C=C bonds are the basis of certain thermosetting resins and are often used at low levels in free-radical copolymerizations [6]. For example, itaconic acid ($\text{R} = \text{X} = \text{CO}_2\text{H}$) is often used in the preparation of emulsion copolymers for coating and adhesive applications [7, 8]. Other important uses of monomers containing allylic C=C bonds are for preparation of crosslinked polymers

and for grafting of phases at interfaces in multi-phase polymers [9–14].

The work reported in this paper was performed in support of a programme of research into rubber-toughened poly(methyl methacrylate) materials. These materials contain sub-micron size, multi-layer particles which are prepared at 80°C by sequential emulsion polymerization [15, 16]. The particles have two to four alternating rubbery and glassy layers, each of which is both crosslinked, and grafted at the internal interfaces, using allyl methacrylate ($\text{R} = \text{H}$ and $\text{X} = \text{O}-\text{CO}-\text{CMe}=\text{CH}_2$) at levels in the range 0.1–3.0 mol% based upon the basic comonomer mixtures forming the bulk of the phases. The basic comonomer mixture used for the rubbery layers comprises 78.2 mol% n-butyl acrylate and 21.8 mol% styrene, and that used for the glassy layers comprises 94.9 mol% methyl methacrylate and 5.1 mol% ethyl acrylate. In order to understand, and make predictions about, these complex copolymerizations, reliable values of monomer reactivity ratios are required for each individual comonomer pair.

The determination of reactivity ratios by direct studies of copolymerizations of allyl methacrylate is impractical due to the low reactivity of allylic C=C bonds and the fixed initial 1:1 stoichiometry of methacrylic to allylic C=C bonds. In order to obtain reliable values of reactivity ratios, high mole fractions of allylic C=C bonds are required in the initial comonomer mixtures to give copolymers with measurable mole fractions of repeat units from allyl polymerization. Hence, it is necessary to consider

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reactivity ratios for related, model copolymerizations such as those of allyl acetate which may then be taken as representative of the allylic C=C bond in allyl methacrylate. Values of reactivity ratios are available [17, 18] for copolymerization of allyl acetate with methyl methacrylate, styrene and methyl acrylate, though not for its copolymerization with *n*-butyl acrylate. The published values, however, cannot be used with confidence. In the one case [17], the values were either:

- (i) quoted without giving details of the procedures used for their determination; or
- (ii) determined from a single experiment assuming ideal behaviour (i.e. that the product of the reactivity ratios is unity) and without reporting details of the method for evaluation of copolymer composition.

In the other case [18], feed compositions with low mole fractions of allyl acetate were employed together with unsatisfactory methods for both composition determination and evaluation of reactivity ratios.

The principal objective of the work reported here, therefore, was to determine reliable values of the reactivity ratios for model copolymerizations of allyl acetate with methyl methacrylate, *n*-butyl acrylate and styrene. These values could then be used to establish the relative contributions of the methacrylic and allylic C=C bonds in allyl methacrylate to crosslinking/graftlinking and to gain a better understanding of the mechanism of graftlinking of phases at interfaces in multi-phase polymers.

A subsidiary objective of the studies was to investigate the extent of cyclopolymerization [19] in polymerizations of allyl methacrylate. This has previously been invoked [20, 21], though unequivocal evidence for the existence of the resulting in-chain lactone rings was not presented.

EXPERIMENTAL PROCEDURES

Materials

With the exceptions of allyl acetate (Aldrich) and ethylene dimethacrylate (BDH), polymerization grade monomers were supplied by ICI. The monomers were purified by vacuum distillation under nitrogen and were individually degassed by freeze-thaw cycling under high vacuum just prior to use. The refractive indices of the purified monomers were measured at 20°C using a Pulfrich refractometer and the sodium D-line, and in each case were found to agree with literature values to within ± 0.002 or better, thus confirming their purity (see Table 1). Toluene (BDH), methanol (BDH) and 1,4-dioxane (BDH) were purified by distillation at atmospheric pressure under nitrogen. 2,2'-Azobis(2-cyanopropane) (BDH) was purified by preparing a solution in methanol, filtering the solution and then adding deionized water to precipitate the 2,2'-azobis(2-cyanopropane) which was dried under vacuum at room temperature. Benzoyl peroxide (Aldrich) was purified in the same way as described for 2,2'-azobis(2-cyanopropane).

Copolymerizations of allyl acetate

Allyl acetate was copolymerized with (a) methyl methacrylate, (b) *n*-butyl acrylate and (c) styrene using 2,2'-azobis(2-cyanopropane) at 0.002–0.02% by weight of the total comonomer mixture (*ca* 20 g). A summary of the copolymerizations carried out is given in Table 2, together

Table 1. Refractive indices of the purified monomers

Monomer	Refractive index, n_D^{20}	
	Measured value	Literature value ^a
Allyl acetate	1.4024	1.4040
Allyl methacrylate	1.4357	1.4360
<i>n</i> -Butyl acrylate	1.4176	1.4160
Ethyl acrylate	1.4058	1.4068
Ethylene dimethacrylate	1.4522	1.4525
Methyl methacrylate	1.4146	1.4146
Styrene	1.5450	1.5468

^aThe value for allyl methacrylate is that reported in Ref. [29], all other values are taken from Ref. [30].

with the actual quantities used in each reaction. The following general procedure was employed. Allyl acetate, the comonomer and 2,2'-azobis(2-cyanopropane) were accurately weighed into a thick-walled glass tube. The mixture was then frozen by placing the tube in liquid nitrogen before sealing the tube under vacuum. Polymerization was effected by placing the sealed tube in a thermostatted water bath at $80.0 \pm 0.1^\circ\text{C}$ for a period of 15–90 min. The reactions were terminated by cooling to room temperature, breaking open the tube and pouring the contents into a three-fold excess of methanol. The precipitated copolymer was isolated by filtration, dissolved in chloroform and then re-precipitated into methanol. The precipitate was collected by filtration through a No. 3 sinter and dried to constant weight under vacuum at room temperature.

Quantitative determination of yields proved to be difficult. The low mass yields (25–250 mg) in the copolymerizations involving methyl methacrylate and styrene led to considerable difficulties in quantitative work-up of the copolymers. The copolymerizations involving *n*-butyl acrylate gave higher mass yields (1–2 g), but the copolymers proved extremely difficult to work-up quantitatively due to their low glass transition temperatures. Hence, best estimates of yields have been used when determining the significance of composition drift in the evaluation of reactivity ratios.

Polymerizations of allyl methacrylate

Two samples of poly(allyl methacrylate), designated PAM1 and PAM2, were prepared by bulk polymerization of allyl methacrylate (*ca* 18 g) at $80.0 \pm 0.1^\circ\text{C}$ for 15 min using 2,2'-azobis(2-cyanopropane) (0.002 g) as initiator. The short reaction time was employed in order to obtain soluble samples of poly(allyl methacrylate). The procedure used was

Table 2. Summary of the copolymerizations performed for determination of reactivity ratios^a

Designation	AA/g ^b	MMA/g ^b	BA/g ^b	S/g ^b	AZBN/g ^b	f_A^c
90A/10M ^d	17.035	2.082	—	—	0.010	0.891
85A/15M ^e	16.953	2.999	—	—	0.020	0.850
50A/50M ^f	20.019	19.989	—	—	0.004	0.500
85A/15B	16.317	—	4.307	—	0.008	0.829
80A/20B	15.362	—	4.846	—	0.012	0.802
70A/30B	15.191	—	7.100	—	0.010	0.732
60A/40B	10.893	—	9.290	—	0.010	0.600
90A/10S	17.945	—	—	2.084	0.004	0.899
85A/15S	16.874	—	—	3.100	0.006	0.849
80A/20S	15.948	—	—	4.146	0.002	0.800
75A/25S	14.929	—	—	5.149	0.003	0.751

^aReaction temperature = $80.0 \pm 0.1^\circ\text{C}$; reaction time = 45 min unless otherwise specified.

^bAA = allyl acetate; MMA = methyl methacrylate; BA = *n*-butyl acrylate; S = styrene; AZBN = 2,2'-azobis(2-cyanopropane).

^cInitial mole fraction of allyl groups.

^dReaction time = 90 min.

^eReaction time = 30 min.

^fReaction time = 15 min.

the same as described for the allyl acetate copolymerizations. Similar work-up problems were encountered as with the allyl acetate copolymers, again due to the low mass yields.

Additionally, a solution polymerization of allyl methacrylate (11.026 g, 87.4 mmol) was carried out in 1,4-dioxane (80.013 g, 77.4 cm³) at 60.0 ± 0.1°C using benzoyl peroxide (0.135 g, 0.56 mmol) as initiator for comparison with previous work [20]. The reaction mixture was divided into portions, each being treated in the same way as for the allyl acetate copolymerization. Three samples of poly(allyl methacrylate) were obtained. The first, sample PAM3, was taken after 3 hr reaction, at which time the reaction mixture had just become immobile (visual inspection), and the other two, samples PAM4 and PAM5, after further periods of 1 and 18 hr reaction respectively. For each of these samples the work-up problems were exacerbated by the gelled nature of the product mixture.

Preparation and reaction of a model terpolymer

A model terpolymer containing pendant allylic and methacrylic C=C bonds was prepared as follows. Allyl methacrylate (61.57 g, 0.489 mol), methyl methacrylate (39.09 g, 0.391 mol), ethylene dimethacrylate (19.35 g, 0.098 mol) and toluene (1200 g) were added to a 2 dm³ flanged reaction vessel which was equipped with a gas inlet tube, a condenser, and a mechanically-driven paddle stirrer. The vessel was placed in a thermostatted water bath at 80°C and a flowing nitrogen atmosphere established whilst the reaction mixture heated to the bath temperature. A solution of 2,2'-azobis(2-cyanopropane) (0.02 g, 0.12 mmol) in toluene (10 g) was then added and the reaction allowed to proceed for 3 hr. Methanol (200 g) was added to quench the reaction and the resulting mixture poured into a three-fold excess of methanol. The precipitated terpolymer was collected by filtration, dissolved in toluene and then re-precipitated into excess methanol. The product was collected by filtration through a No. 3 sinter and dried to constant weight under vacuum at room temperature to yield 8.41 g of terpolymer.

A small-scale reaction of the terpolymer (5.196 g) with ethyl acrylate (0.481 g) in toluene (46.8 g) was carried out at 80.0 ± 0.1°C using 2,2'-azobis(2-cyanopropane) (0.022 g) as initiator. The reaction mixture was divided into four portions, each being sealed under vacuum in a thick-walled glass tube before carrying out the reaction. The four samples were allowed to react for 1, 2, 4 and 6 hr respectively before terminating the polymerization and isolating the product in the way described for the allyl acetate copolymerizations.

NMR spectroscopy

¹H-NMR spectra were obtained using a Bruker Spectrospin AC300E spectrometer operating at 300 MHz. ¹³C-NMR spectra were obtained using the AC300E spectrometer and a Varian Associates XL-300 spectrometer both operating at 75.5 MHz, and a Varian Associates Unity 500 spectrometer operating at 125.5 MHz. All spectra were recorded at room temperature. Samples were made up as solutions in CDCl₃ containing 25–100 mg polymer in 1 cm³ solvent. Chemical shifts were referenced to the solvent, taken to lie at δ_H = 7.25 ppm and δ_C = 77.0 ppm. ¹H spectra were run with a sufficiently large pulse interval to allow full relaxation of all peaks between pulses in order to ensure quantitative accuracy. However, in order to maximize the signal-to-noise ratio in a given time, ¹³C spectra were normally run with continuous proton decoupling using a pulse interval of 0.5 sec and a flip angle of 45°. Under these conditions, the relative intensities do not necessarily reflect the relative abundance of each type of carbon because of differential relaxation times and nuclear Overhauser enhancements (NOE). In particular, the intensities of primary and quaternary carbons are underestimated relative to CH and CH₂ carbons. However, compositional data quoted

below were obtained by comparing the intensities of like carbons, so relative intensities do reflect the relative abundance of the corresponding type of carbon. In order to check the quantitative accuracy of these fast pulse spectra, some samples were also run with NOE suppression by gated decoupling and with a pulse interval of 10.5 sec to allow complete recovery of all carbons.

To assist in assigning the ¹³C spectra, the DEPT technique [22] was used to determine the multiplicity of the peaks, i.e. whether that carbon was primary, secondary, tertiary or quaternary.

RESULTS AND DISCUSSION

Determination of reactivity ratios

Reactivity ratios were derived either from copolymer compositions or from the monomer dyad probability distribution depending on the information available from the NMR spectra.

For composition data for a copolymer of monomers A and B, the reactivity ratios were obtained by a direct computer fit [23] of the composition data to the copolymer composition equation [24]:

$$F_A = \{r_A f_A^2 + f_A f_B\} / \{r_A f_A^2 + 2f_A f_B + r_B f_B^2\} \quad (f_B = 1 - f_A) \quad (1)$$

where F_A is the mole fraction of monomer A repeat units in the copolymer, f_A is the mole fraction of monomer A in the feed, and r_A and r_B are the reactivity ratios. Account was taken of composition drift by stepping through the conversion range in increments of 0.2% and adjusting the feed composition each time before averaging the calculated compositions over the complete conversion range.

In the case of the dyad probability distribution analysis, the reactivity ratios were obtained directly from the relations:

$$(AA) = w(1 - u)/(u + w) \quad (2a)$$

$$(AB) = 2uw/(u + w) \quad (2b)$$

$$(BB) = u(1 - w)/(u + w) \quad (2c)$$

where (X) is the probability of dyad X and u and w are the first-order Markov probabilities for respectively the addition of B to a chain ending in A, and the addition of A to a chain ending in B. The parameters u and w are given by:

$$u = f_B/(r_A f_A + f_B) \quad (3a)$$

$$w = f_A/(r_B f_B + f_A) \quad (3b)$$

As described below, the copolymers for which a dyad analysis could be carried out were prepared to very low conversion, so no account was taken of composition drift.

Allyl acetate (A)/methyl methacrylate (M) copolymers. Figure 1 shows the NOE-suppressed ¹³C spectrum of sample 90A/10M prepared to 1% conversion from a monomer feed consisting of 89.1 mol% A. Apart from a small peak from residual methanol remaining from the work-up procedure, the spectra show no evidence of peaks other than those attributable to the copolymer. In spite of the preponderance of A in the feed, the major peaks resemble the spectrum of poly(methyl methacrylate), indicating a very strong preference for addition of M. There are

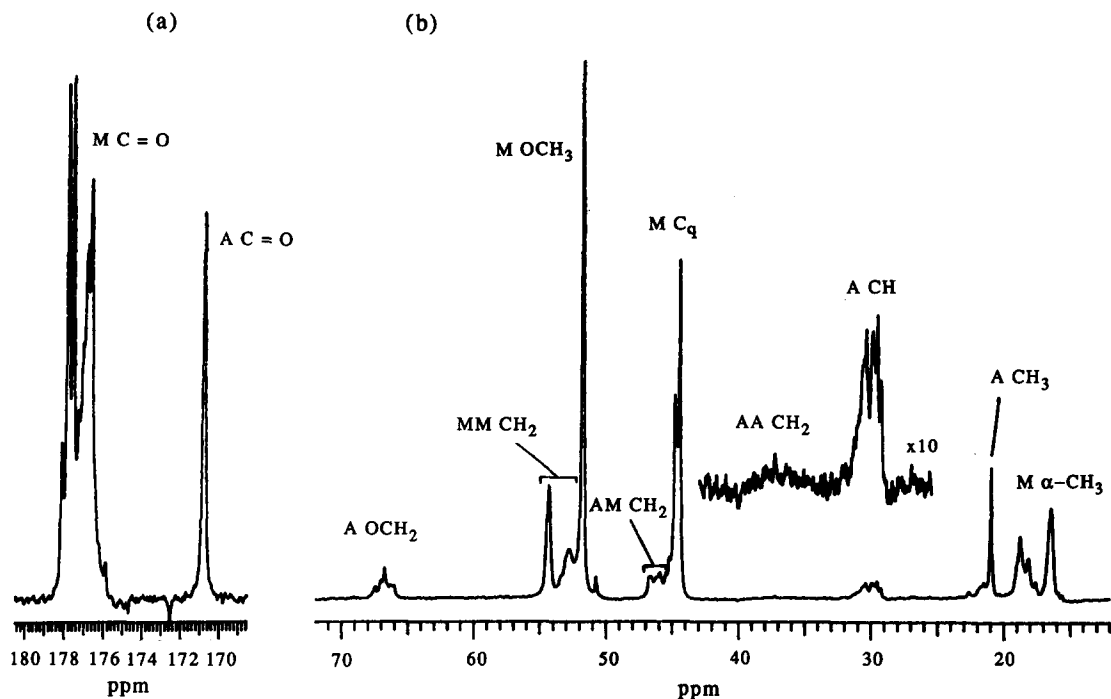


Fig. 1. The ^{13}C -NMR spectrum of a copolymer of allyl acetate and methyl methacrylate, sample 90A/10M. (a) Carbonyl region, (b) saturated carbon region. Resonances from allyl acetate units are identified by A, and those from methyl methacrylate units by M.

several clearly resolved resonances characteristic of each repeat unit, such as the M carbonyl at 176–178 ppm, the A carbonyl at 170.4 ppm, the A OCH_2 at 66–68 ppm, the M OCH_3 at 51.8 ppm and the A CH at 29–31 ppm; the composition of the polymer could readily be obtained from the relative integrals of these peaks. Most of these regions are split into a number of incompletely resolved peaks due to the effects of irregular stereochemistry and sequence structure. The backbone CH_2 carbons, however, show a very strong dependence on the structure of the adjacent monomer repeat units, being distributed over three distinct absorption regions assigned to (AA) dyads (35–39 ppm), (AM) dyads (45.5–47 ppm) and (MM) dyads (52–55 ppm). These assignments were made on the basis of four arguments: first, the internal consistency of intensities within one copolymer spectrum; second, the variation of the intensities of the three CH_2 signals with polymer composition; third, comparison with the spectrum of M homopolymer; and fourth, comparison with the expected chemical shifts calculated from well-established substituent chemical shift increments [25]. Although the (AA) dyad CH_2 peak is very small, its assignment as indicated in Fig. 1 is reliable in view of the flatness of the spectrum baseline elsewhere.

The observation of distinct dyad resonances allows the determination of reactivity ratios from the dyad sequence distribution. In view of the low conversions (<1.5%), as well as the large uncertainties in determining the dyad probabilities [particularly the (AA) dyad], composition drift was neglected in the calculations. Table 3 gives the dyad distribution, the feed

composition and the reactivity ratios derived using equations (2) and (3) for the two samples, 85A/15M and 90A/10M, for which the (AA) dyad resonance could be distinguished. Allowing for estimated experimental uncertainties in the dyad probabilities of ca 30% in (AA), 10% in (AM) and 5% in (MM) yields uncertainties of the order of 35% in r_A and 15% in r_M . The two values each of r_A and r_M in Table 3 differ by less than these amounts, and average $r_A = 0.024 \pm 0.009$ and $r_M = 41 \pm 6$. The product $r_A r_M$ is unity within experimental error, indicating that the copolymerization conforms to Bernoullian statistics whereby the probability of adding a particular monomer is independent of the unit at the chain end.

For sample 50A/50M, the (AA) dyad probability was too low to measure. However, the composition of this copolymer may be used as a check on the reactivity ratios from the dyad distribution. Using the mean ratios above, the calculated copolymer composition for an equimolar feed is 2.3 mol% A, in

Table 3. Dyad probability distribution and derived reactivity ratios for copolymerization of allyl acetate (A) with methyl methacrylate (M)

Parameter	Copolymer sample	
	85A/15M	90A/10M
f_A	0.850	0.891
(AA)	0.010	0.034
(AM)	0.207	0.285
(MM)	0.779	0.681
r_A	0.018	0.029
r_M	43	39

excellent agreement with the experimental value of 2.7 ± 0.3 mol% A.

Allyl acetate (A)/n-butyl acrylate (B) copolymers. Figures 2 and 3 show respectively the ^1H - and ^{13}C -NMR spectra of sample 80A/20B prepared using a monomer feed of 80.2 mol% A. Unlike the previous system, these spectra provide no information on the dyad sequence distribution; the peaks observed were assignable only to repeat units from a particular monomer, or to both, so that only the copolymer composition could be obtained. There are noticeable peaks from residual monomer (mainly B) which coincide with some of the polymer peaks. However, enough polymer peaks are sufficiently resolved from monomer to permit a quantitative analysis of the composition. In the ^1H spectrum, the most convenient method was to use the relative intensities of the A CH_3COO — peak at 2.04 ppm and the combined (A + B) $-\text{OCH}_2-$ peak at 3.8–4.1 ppm. In the ^{13}C spectrum, the distinct A and B carbonyl signals were used. Copolymer compositions given in Table 4 are averages of the ^1H and ^{13}C values.

Because of difficulties in effecting a quantitative isolation of the copolymer, the degree of conversion was not accurately known, but in each case was estimated to be $7 \pm 3\%$. The simulation of the dependence of copolymer composition on feed composition, based upon equation (1), was, therefore, carried out for the estimated extreme values. Simulations were also carried out using the composition data for each monomer; details are given in Table 4.

There is a large variation in the best-fit values of r_A , depending on the conversion and which monomer is used to express the compositions. The calculations yield average reactivity ratios of $r_A = 0.04 \pm 0.02$ and $r_B = 11.7 \pm 1.0$.

Allyl acetate (A)/styrene (S) copolymers. Figures 4 and 5 show the ^1H - and ^{13}C -NMR spectra respectively of sample 90A/10S prepared using a monomer feed of 89.9 mol% A. As in the n-butyl acrylate system, no information on the sequence distribution is resolved, but the copolymer compositions are readily obtainable from the intensity of the A $-\text{CH}_2\text{O}-$ resonances relative to the S aromatic resonances. The copolymer compositions used for the evaluation of reactivity ratios were averages of the ^1H and ^{13}C values, and are given in Table 5 together with details of the composition simulation. Since each of the copolymers was prepared to a conversion of ca 0.2%, composition drift was not taken into account in the calculations. The values obtained for the reactivity ratios are effectively independent of which type of repeat unit, A or S, is used to specify composition and, with maximum uncertainties, are: $r_A = 0.021 \pm 0.001$ and $r_S = 66 \pm 4$.

Discussion. Since the objective of the experiments described above was to determine reliable values of reactivity ratios, it was essential to obtain copolymers containing measurable contents of allyl acetate repeat units; hence the use of high mole fractions of allyl acetate in the comonomer mixtures. However, even with feed mixtures comprising 60–90 mol% allyl

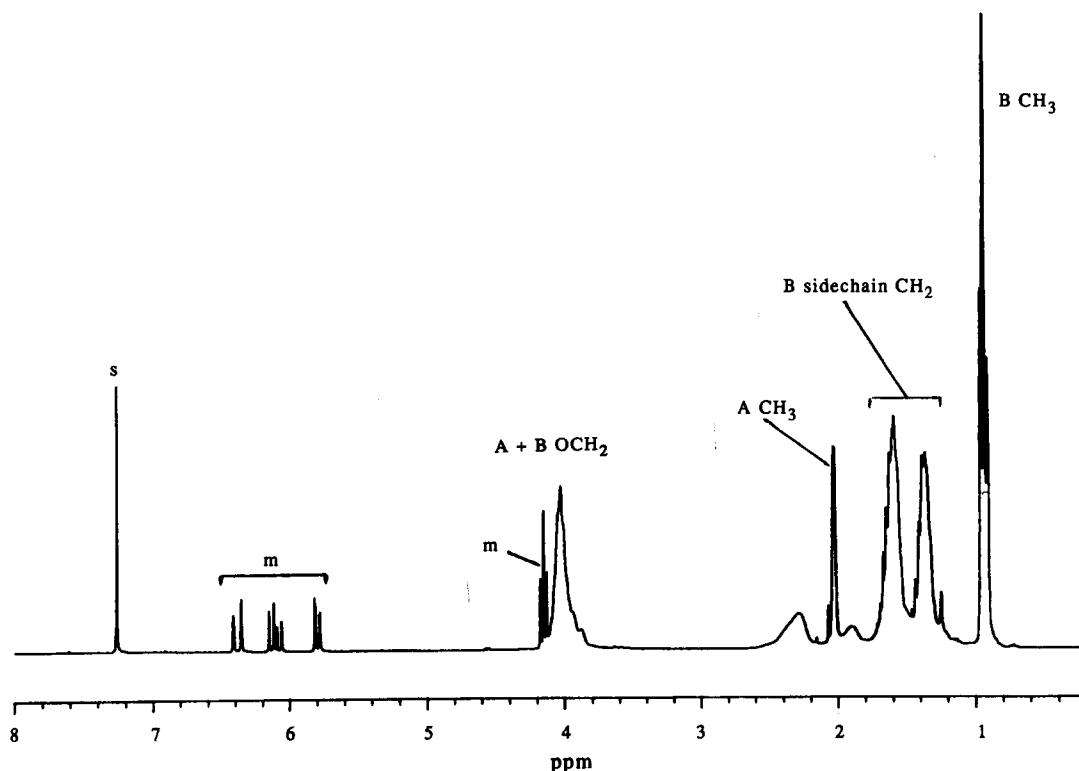


Fig. 2. The ^1H -NMR spectrum of a copolymer of allyl acetate and n-butyl acrylate, sample 80A/20B. Resonances from allyl acetate units are identified by A, and those from n-butyl acrylate units by B. The backbone protons give several broad peaks in the range 1.4–2.5 ppm. The labels m and s indicate peaks from residual B monomer and CHCl_3 impurity in the NMR solvent respectively.

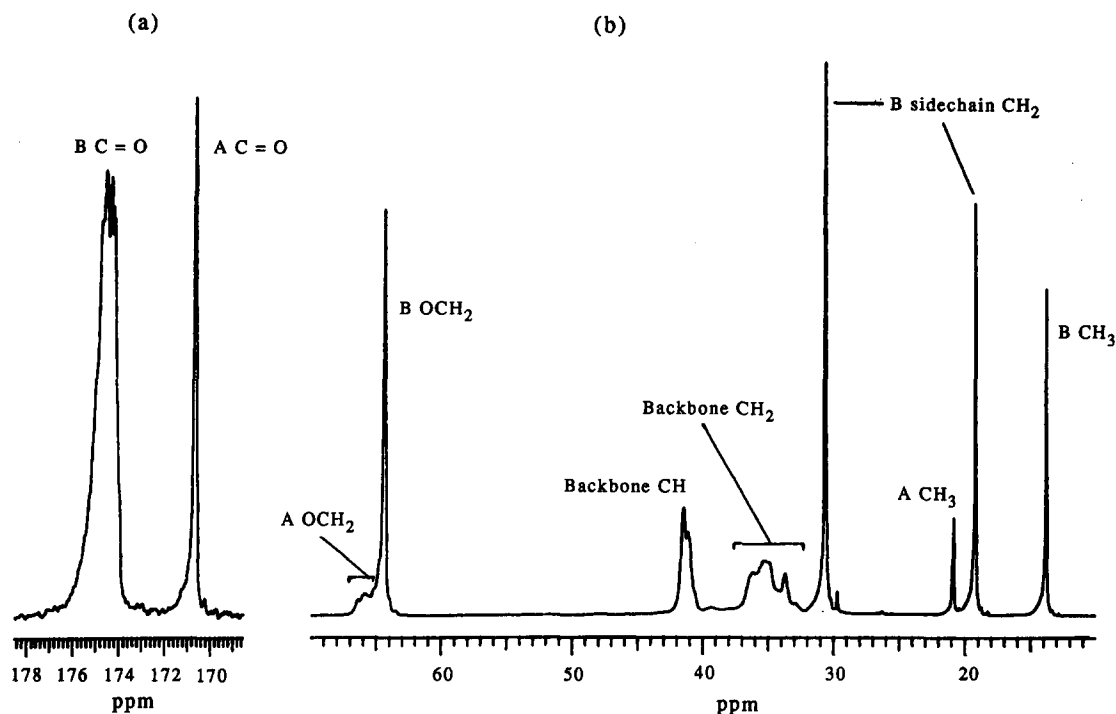


Fig. 3. The ¹³C-NMR spectrum of a copolymer of allyl acetate and n-butyl acrylate, sample 80A/20B. (a) Carbonyl region, (b) saturated carbon region. Resonances from allyl acetate units are identified by A, and those from n-butyl acrylate units by B.

acetate, the mole fractions of allyl acetate repeat units in the copolymers formed were relatively low, thereby leading to significant uncertainties in the determination of copolymer composition and in the resulting values of the reactivity ratios, especially those for allyl acetate. Experiments designed to improve the accuracy of the measurements of composition, by increasing the mole fraction of allyl acetate repeat units in the copolymers through the use of very high mole fractions (i.e. > 90 mol%) of allyl acetate in the comonomer mixtures, proved to be impractical due to the extremely low mass yields arising as a consequence of autoinhibition. Thus, the range of mole fractions of allyl acetate employed in the copolymerizations included the highest, experimentally-realistic values and sufficient differences between individual experiments so that the differences in the compositions of the resulting copolymers were significantly

greater than the errors in the determination of copolymer composition. In this way, the errors in the determinations of reactivity ratios have been minimized.

There is a consistent increase in the value of the reactivity ratio for allyl acetate, and a decrease in that for the comonomer, as the comonomer changes from styrene to methyl methacrylate to n-butyl acrylate. This is the order of reactivity expected on the basis of the number and type of substituents, and shows that the values of the reactivity ratios for the model copolymerizations are consistent with each other.

In summary, the reactivity ratios have been determined using optimum mole fractions of allyl acetate in the comonomer mixtures and are self-consistent. On this basis, the values of the reactivity ratios obtained for the model copolymerizations are considered to be far more accurate than those reported

Table 4. Comonomer-feed and copolymer compositions, and derived reactivity ratios for copolymerization of allyl acetate (A) with n-butyl acrylate (B)

Copolymer sample	f_A	F_A (exp)	F_A (calc) for conversion ^a		F_A (calc) for conversion ^b	
			4%	10%	4%	10%
85A/15B	0.829	0.296	0.278	0.278	0.286	0.286
80A/20B	0.802	0.236	0.248	0.248	0.251	0.251
70A/30B	0.732	0.183	0.188	0.188	0.185	0.185
60A/40B	0.600	0.121	0.118	0.117	0.111	0.111
r_A			0.034	0.016	0.064	0.038
r_B			10.7	11.2	12.1	12.6
RMS deviation (%)			4.4	4.5	1.3	1.3

^aMole fraction of A used in fitting.

^bMole fraction of B used in fitting.

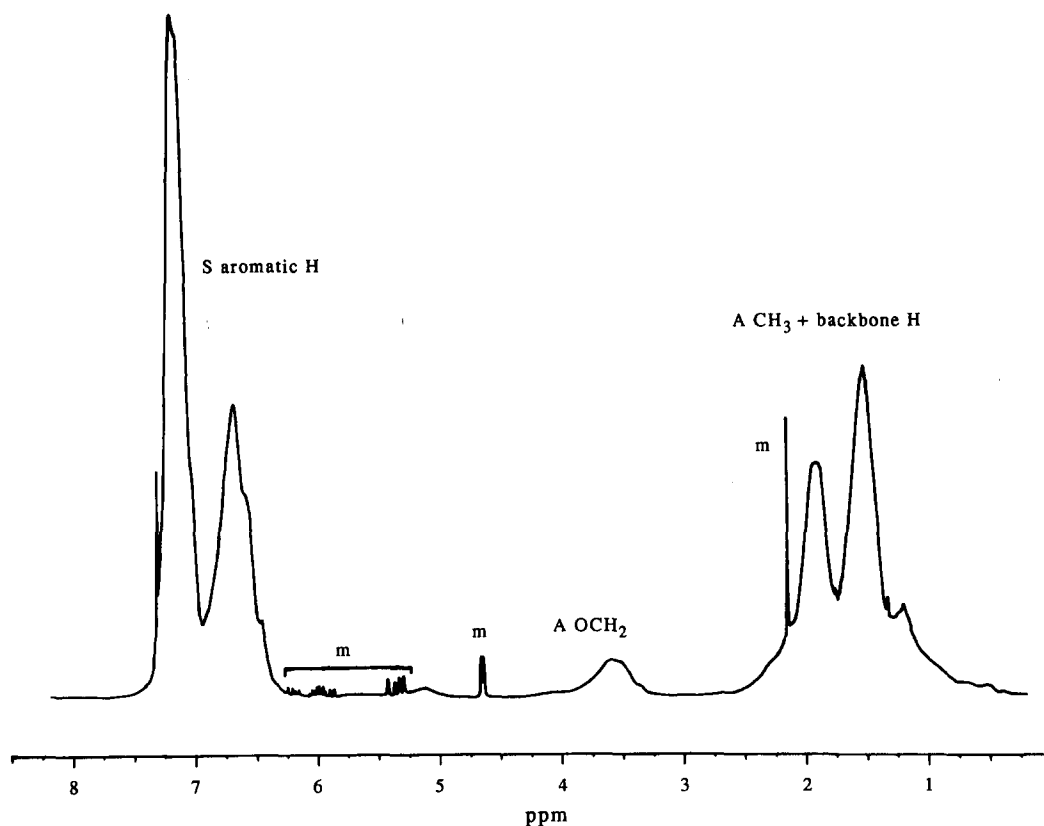


Fig. 4. The ^1H -NMR spectrum of a copolymer of allyl acetate and styrene, sample 90A/10S. Resonances from allyl acetate units are identified by A, and those from styrene units by S. The label m indicates peaks from residual monomer.

previously [17, 18] and sufficiently reliable to justify prediction of the polymerization behaviour of allyl methacrylate.

Poly(allyl methacrylate)

Structure. The ^{13}C -NMR spectrum of sample PAM1 of poly(allyl methacrylate) is shown in Fig. 6. The principal features of the spectrum which are of significance in determining the mode of polymerization are these:

- the CH_3 resonances at 16–22 ppm, the quaternary carbon resonance at 45 ppm, the CH_2 resonances at 50–55 ppm and the carbonyl resonances at 175–178 ppm are all almost identical in position, form and relative intensity to resonances in the spectrum of poly(methyl methacrylate) prepared by free-radical polymerization;
- there is an intense peak at 66 ppm attributable to a CH_2O carbon and a weak CH peak at 30 ppm, but apart from the peaks mentioned in (a) there are no other significant aliphatic resonances;
- there are two major olefinic peaks, a CH_2 carbon at 118.5 ppm and a CH at 132 ppm, which are almost identical in chemical shift to the olefinic peaks in allyl acetate and which have essentially the same intensity (in NOE-suppressed spectra) as the peaks mentioned in (a);

- there are minor olefinic peaks at 125.5 ppm (CH_2) and 136.2 ppm (quaternary), and a minor carbonyl peak at 167.3 ppm, which are almost identical in chemical shift to the olefinic and carbonyl peaks in methyl methacrylate.

These observations indicate that the principal polymerization mode of allyl methacrylate under the conditions employed here is the sequential polymerization of methacrylic $\text{C}=\text{C}$ bonds to give a chain with pendant allyl ester groups. The minor olefinic, carbonyl and aliphatic CH peaks indicate a small degree of polymerization of the allyl group giving a backbone $-\text{CH}_2-\text{CH}-$ unit and a pendant methacrylate group. Following the discussion of allyl acetate/methyl methacrylate copolymers above, the resonances from CH_2 carbons flanked by carbons one of which bears a methacrylate-containing side-group and the other an allyl ester-containing side-group, would be expected at a similar chemical shift (ca 45–47 ppm) to the CH_2 carbons in the AM dyad in the allyl acetate/methyl methacrylate copolymers. However these CH_2 peaks are not clearly visible in the normal ^{13}C spectrum because the slight difference in environment in poly(allyl methacrylate) results in a small low frequency shift compared to the copolymer to a position where they are obscured by the quaternary carbon resonance of polymerized methacrylate groups at 45 ppm. The peaks are clearly detected using the DEPT technique [22] which effectively

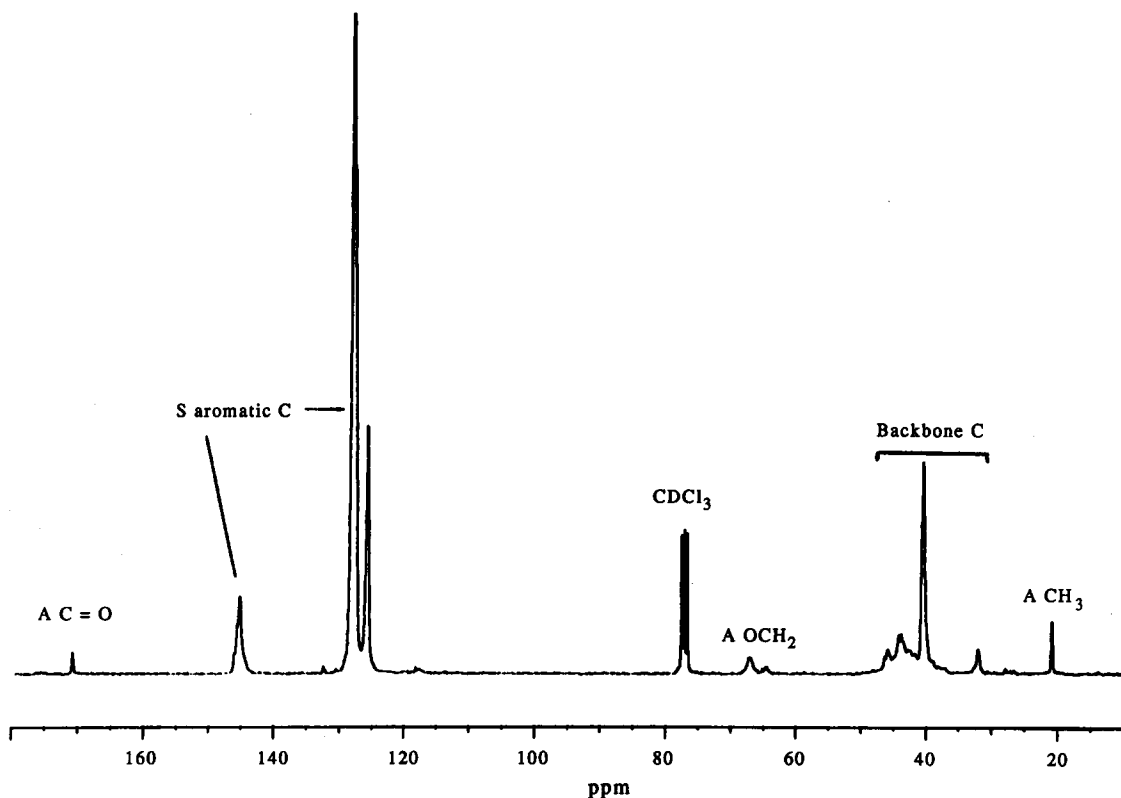


Fig. 5. The ^{13}C -NMR spectrum of a copolymer of allyl acetate and styrene, sample 90A/10S. Resonances from allyl acetate units are identified by A, and those from styrene units by S.

eliminates quaternary carbon resonances, as shown in Fig. 6(b). The intensity of these CH_2 peaks is approximately twice that of the CH peak at 30 ppm, consistent with a chain structure consisting of infrequent polymerized allyl groups in a poly(methacrylate) chain. A summary of the peak assignments is given in Table 6.

As noted in the Introduction, it has been suggested [20, 21] that allyl methacrylate may undergo cyclopolymerization reactions leading to the formation of in-chain lactone rings with the following structures:

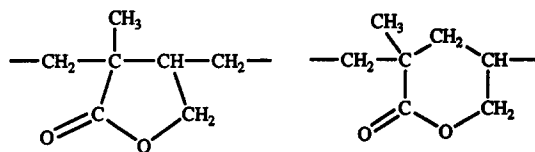


Table 5. Comonomer-feed and copolymer compositions, and derived reactivity ratios for copolymerization of allyl acetate (A) with styrene (S)

Copolymer sample	f_A	$F_A(\text{exp})$	$F_A(\text{calc})^a$	$F_A(\text{calc})^b$
90A/10S	0.899	0.122	0.123	0.124
85A/15S	0.849	0.084	0.080	0.081
80A/20S	0.800	0.053	0.058	0.058
75A/25S	0.751	0.047	0.044	0.045
r_A			0.021	0.021
r_S			67	66
RMS deviation (%)			6.0	0.4

^aMole fraction of A used in fitting.

^bMole fraction of S used in fitting.

The occurrence of these rings should be readily detectable by ^{13}C -NMR by a decrease in the intensity of the allyl olefinic carbon signals and by an increase in the number of saturated carbon signals. As mentioned above, the intensity of the allyl olefinic resonances was almost equal to that of the carbonyl, $\alpha\text{-CH}_3$, and other resonances. As far as the possible observation of additional saturated carbon signals is concerned, the ring OCH_2 carbons should provide a diagnostic test for the lactone structures. In the prototype rings of γ -butyrolactone and δ -valerolactone, the OCH_2 carbons occur at 68.8 and 69.4 ppm respectively [26]. Using substituent chemical shift increment parameters [25], it is calculated that incorporation into a polymer chain in the manner indicated would shift both these carbons to the region of 72 ± 4 ppm. Since no peaks are observed in this region for any of the samples of poly(allyl methacrylate) prepared (e.g. see Fig. 6), the unambiguous conclusion from the present studies is that cyclopolymerization is insignificant.

The above conclusion, however, is in disagreement with that of Matsumoto *et al.* [21], who reported that in benzonitrile solution at 80°C some 7% of monomer units underwent cyclopolymerization. The extent of cyclopolymerization was measured indirectly by determining the residual unsaturation in the polymer iodometrically rather than by the more reliable, direct NMR method. It is noteworthy that the ^{13}C -NMR spectrum of poly(allyl methacrylate) published by Matsumoto *et al.* shows the same major peaks as the spectrum in Fig. 6 and, more signifi-

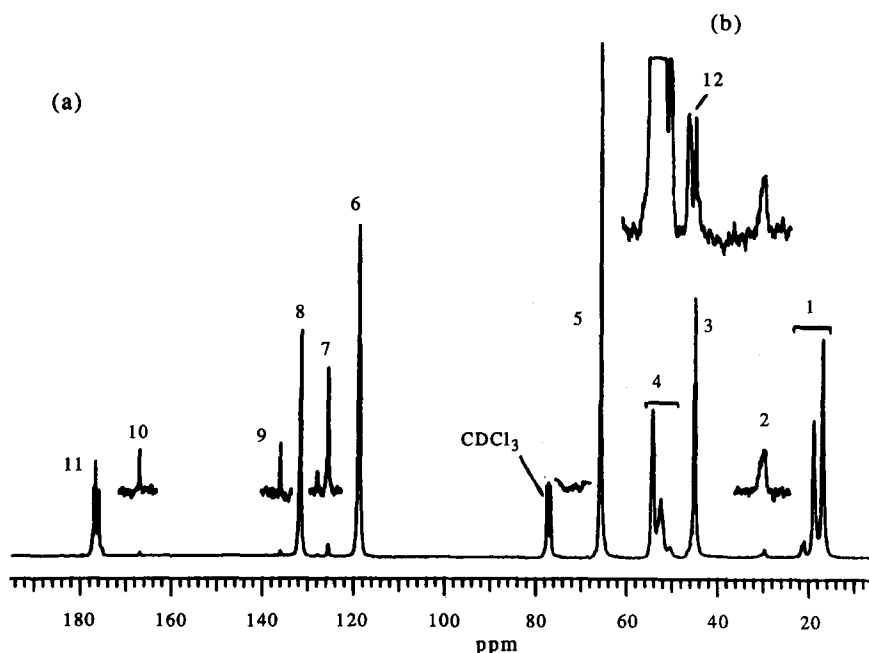


Fig. 6. The ^{13}C -NMR spectrum of poly(allyl methacrylate) sample PAM1. (a) "Normal" spectrum, vertical expansions $\times 10$; (b) part of a DEPT spectrum showing the AM dyad CH_2 signal at 46 ppm underlying the backbone C_q signal, as discussed in the text. Peak assignments are given in Table 6.

cantly, an absence of the expected peaks for lactone OCH_2 carbons. No attempt was apparently made to analyse the spectrum quantitatively, nor were any of the minor peaks identified. The conclusion of Matsumoto *et al.* is, therefore, contradicted by their ^{13}C -NMR data.

From the ^{13}C spectra of the poly(allyl methacrylate) samples, it is possible to determine several quantities characterizing the polymer structure. The following are the most direct:

- the fraction of all polymerized units which are allyl, determined from the intensity of the backbone CH peak relative to the total backbone carbon intensity, denoted F_A^p ;
- the fraction of carbonyl carbons existing as unreacted methacrylate, determined from the intensities of the unreacted methacrylate

$\text{C}=\text{O}$ peak and the reacted methacrylate $\text{C}=\text{O}$ peak, denoted F_M^u ;

- the fraction of unreacted groups which are methacrylate, determined from the intensities of the unreacted methacrylate olefinic carbons and the unreacted allyl olefinic carbons, denoted F_M^{olef} .

For all poly(allyl methacrylate) samples except those prepared to very low conversion, it was found that F_A^p was considerably greater than both F_M^u and F_M^{olef} , indicating that there is a high probability of further polymerization of pendant methacrylate groups. The polymer must, therefore, be regarded as a "terpolymer" consisting of the units:

- A reacted, M unreacted—denoted A_p ;
- M reacted, A unreacted—denoted M_p ;
- both A and M reacted—denoted AM_p .

Designating the fractions of these units in the polymer by $[A_p]$, $[M_p]$ and $[AM_p]$ respectively, the quantities F_A^p , F_M^u and F_M^{olef} are given by

$$F_A^p = ([A_p] + [AM_p]) / ([A_p] + [M_p] + 2[AM_p]) \quad (4a)$$

$$F_M^u = [A_p] \quad (4b)$$

$$F_M^{\text{olef}} = [A_p] / ([A_p] + [M_p]) \quad (4c)$$

The values of $[A_p]$, $[M_p]$ and $[AM_p]$ can be determined by solving simultaneously equations (4a), (4b) and (4c) together with the necessary relationship

$$[A_p] + [M_p] + [AM_p] = 1. \quad (4d)$$

The values obtained for the samples which gave resolvable spectra are given in Table 7. In each case, the value of $[M_p]$ is very high whilst the values of $[A_p]$ and $[AM_p]$ are very low. For PAM1 and PAM2 $[A_p] > [AM_p]$, whereas for PAM3 $[A_p] < [AM_p]$. This

Table 6. Peak assignments in the ^{13}C -NMR spectrum of poly(allyl methacrylate), sample PAM1 (Fig. 6). Allylic and methacrylic groups are identified by A and M respectively. Polymerized groups are indicated by the subscript p, and unpolymerized groups by the subscript u

Peak	Chemical shift (ppm)	Assignment
1	16–22	M α - CH_3
2	30	A_p backbone CH
3	44–46	M_p backbone C_q
4	50–56	M_p backbone CH_2
5	65.8	A OCH_2
6	119	A_u olefinic CH_2
7	125.5	M_u olefinic CH_2
8	132	A_u olefinic CH
9	136	M_u olefinic C_q
10	167	M_u $\text{C}=\text{O}$
11	175–178	M_p $\text{C}=\text{O}$
12	46	AM dyad CH_2 (see text)

Table 7. The compositions of the poly(allyl methacrylate) samples*

Sample	[A _p]	[M _p]	[AM _p]
PAM1	0.024	0.976	0
PAM2	0.021	0.968	0.011
PAM3	0.011	0.965	0.024

*The quantities [A_p], [M_p] and [AM_p] are defined in the text, together with the method of calculation.

observation is significant, as is discussed below, and correlates with the higher monomer conversion achieved in the preparation of PAM3.

Simulation of allyl methacrylate polymerization. Polymerization of allyl methacrylate can be simulated if it is assumed that the reactivity ratios of the allylic and methacrylic C=C bonds are the same as those for the copolymerization of allyl acetate with methyl methacrylate, and that the reactivity of a particular type of olefinic group is unaffected by whether or not the other group has reacted. Although the lack of accurate yields of polymer prevents simulation of the structures of samples PAM1–3 (and hence the testing of the above assumptions), it is nevertheless instructive to consider simulation of allyl methacrylate polymerization over the complete range of conversion of C=C bonds. This has been achieved on the basis of the above assumptions using the following scheme.

At any instant, there are four states for a particular allyl methacrylate molecule: A_p, M_p, AM_p and unreacted monomer, denoted by m. The polymerization was assumed to occur as a series of small steps during which a small amount, δg moles, of all available olefinic groups, A and M, react. The instantaneous composition of the copolymer is given by equation (1) where F_A is the mole fraction of *all* A groups (i.e. in A_p and AM_p units) polymerized in that step and f_A is the mole fraction of *all* free A groups (i.e. in m and M_p units) available for reaction during that step. From equation (1), the amounts of A and M reacting during this step, δA and δM, are given by

$$\delta A = q\delta g/(1 + q) \quad (5a)$$

$$\delta M = \delta g/(1 + q) \quad (5b)$$

where

$$q = y(r_A y + 1)/(y + r_M)$$

and

$$y = (m + M_p)/(m + A_p).$$

Of the free A groups reacting in this small interval, a fraction m/(m + M_p) would be reaction of m to give A_p, and a fraction M_p/(m + M_p) would be reaction of M_p to give AM_p. The free M groups would be similarly partitioned into a fraction m/(m + A_p) arising from reaction of m to give M_p, and a fraction A_p/(m + A_p) arising from reaction of A_p to give AM_p. The changes in the amounts of m, A_p, M_p and AM_p are then given by

$$\delta m = -[m/(m + M_p)]\delta A - [m/(m + A_p)]\delta M \quad (6a)$$

$$\delta A_p = [m/(m + M_p)]\delta A - [A_p/(m + A_p)]\delta M \quad (6b)$$

$$\delta M_p = [m/(m + A_p)]\delta M - [M_p/(m + M_p)]\delta A \quad (6c)$$

$$\delta AM_p = \delta AM_{pM2nd} + \delta AM_{pA2nd} \quad (6d)$$

where δAM_{pM2nd} and δAM_{pA2nd} are the incremental amounts of AM_p formed by polymerization of pendant methacrylic C=C bonds and pendant allylic C=C bonds respectively. These quantities are given by

$$\delta AM_{pM2nd} = [A_p/(m + A_p)]\delta M \quad (6e)$$

and

$$\delta AM_{pA2nd} = [M_p/(m + M_p)]\delta A. \quad (6f)$$

After each step, the values of the incremental quantities were stored, the amounts of m, A_p, M_p and AM_p were updated, the quantity y was re-calculated, and the process repeated until complete conversion of olefinic groups was attained. Finally, at each step, the following fractional quantities were calculated:

- the fractional conversions of C=C bonds and of monomer, denoted C_{olef} and C_{mon} respectively;
- the fractions [A_p], [M_p] and [AM_p];
- the fractions of polymerized side-group allylic and methacrylic C=C bonds, denoted [sA_p] and [sM_p] respectively;
- the fraction of allyl methacrylate polymerized via the allylic C=C bond first, i.e. the fraction of unreacted plus reacted side-group methacrylic C=C bonds, denoted [sM_{u+p}];
- the fraction of AM_p units resulting from polymerization of the allylic C=C bond first, denoted [AM_{pM2nd}];
- the fraction of AM_p units resulting, within a given interval of olefinic group conversion, from polymerization of the allylic C=C bond first, denoted [δAM_{pM2nd}].

Trial calculations showed that for 1 mol of m, the results were independent of the step size for δg ≤ 0.002 mol. The results from the calculations are shown in Figs 7 and 8.

Figure 7 shows how the average composition of the poly(allyl methacrylate) formed is predicted to change with monomer conversion. This clearly demonstrates that until monomer conversions of about 99% are achieved, the expectation is for [M_p]

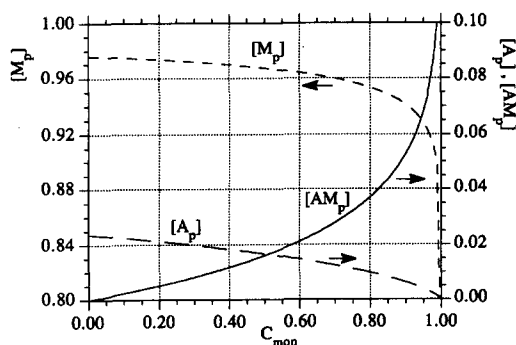


Fig. 7. Theoretical prediction for the variation of the quantities [A_p], [M_p] and [AM_p] with fractional monomer conversion, C_{mon}. See text for definitions of the quantities and details of the calculations.

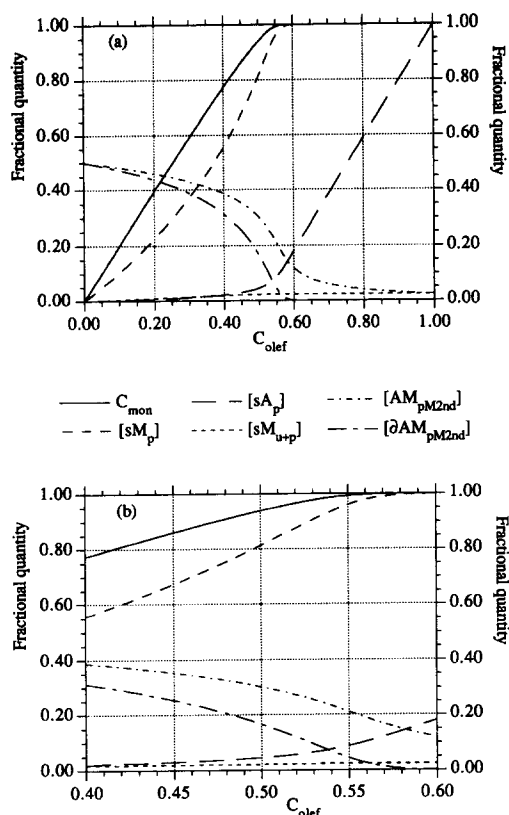


Fig. 8. Theoretical prediction for the variation of the fractional monomer conversion, C_{mon} , and the fractional quantities $[sA_p]$, $[sM_p]$, $[sM_{u+p}]$, $[AM_{pM2nd}]$ and $[dAM_{pM2nd}]$ with fractional conversion of $C=C$ bonds, C_{olef} . (a) Prediction over the complete range of C_{olef} ; (b) expansion of the range of $0.4 \leq C_{\text{olef}} \leq 0.6$. See text for definitions of the quantities and details of the calculations.

to be very high and $[AM_p]$ to be relatively low, in accord with our experimental observations (see Table 7). Figure 7 also shows that the side-group methacrylic $C=C$ bonds should be steadily consumed as monomer conversion increases, reaching complete conversion close to the point of complete conversion of the monomer. Another significant feature is the cross-over in the curves for $[A_p]$ and $[AM_p]$, which occurs at $C_{\text{mon}} \approx 0.5$.

Figure 8 reveals more clearly that complete conversion of the side-group methacrylic $C=C$ bonds should occur almost simultaneously with, though slightly after, complete conversion of the monomer (compare the curves for $[sM_p]$ and C_{mon} in Fig. 8(b)). The fraction of side-group methacrylic $C=C$ bonds either unreacted or polymerized (i.e. of repeat units resulting from polymerization of the allylic $C=C$ bond first) is predicted to be very low throughout the reaction. Thus the disparity in the reactivity ratios ensures that polymerization of the allylic $C=C$ bonds can only become dominant when essentially all of the methacrylic $C=C$ bonds have reacted (see the curve for $[sA_p]$ in Fig. 8(a)). Furthermore, the calculations show that the pendant methacrylic $C=C$ bonds should make a major contribution to branching/crosslinking as long as they exist, even though they

constitute only a very small fraction of the total pendant $C=C$ bonds present (compare the curves for $[sM_{u+p}]$, $[AM_{pM2nd}]$ and $[dAM_{pM2nd}]$ in Fig. 8(a) and (b)). When conversion of the monomer is complete, only pendant allylic $C=C$ bonds remain for further reaction. Since homopolymerization of these groups would be very slow, due to autoinhibition and restrictions upon segmental mobility arising from the crosslinks, the predicted continuous increase in $[sA_p]$ to complete conversion of the allylic $C=C$ bonds is unrealistic and a high proportion of these bonds can be expected to remain unreacted in the final polymer. This is evident in the ^{13}C -NMR spectrum of PAM5 which, although having very broad peaks that prevent accurate quantitative interpretation, is sufficiently well resolved to show that the sample contains a high proportion of unreacted allylic $C=C$ bonds despite the fact that it had undergone a further 18 hr reaction beyond the gel point (which occurred after 3 hr reaction). In this context, it is significant to note that, from the simulation, the sample obtained at the gel point, PAM3, has a composition corresponding to $C_{\text{mon}} \approx 0.7$ (compare the data for PAM3 in Table 7 with the curves in Fig. 7).

Reaction of the model terpolymer

The reactivity ratios measured for copolymerization of allyl acetate with methyl methacrylate and the studies of homopolymerization of allyl methacrylate have shown that reaction of allyl methacrylate takes place predominantly at the methacrylic $C=C$ bond to give polymers with a high mole fraction of pendant allylic $C=C$ bonds and a low mole fraction of pendant methacrylic $C=C$ bonds. Furthermore, it can be inferred that even when the molar ratio of pendant methacrylic to pendant allylic $C=C$ bonds is very low, the methacrylic $C=C$ bonds will contribute significantly to grafting and crosslinking. In order to demonstrate that this inference is correct, reaction of a model terpolymer comprising pendant allylic and methacrylic $C=C$ bonds was investigated.

The terpolymer was prepared by copolymerization of allyl methacrylate with methyl methacrylate and ethylene dimethacrylate using the monomers at mole fractions of 0.50, 0.40 and 0.10 respectively. This composition was chosen as a compromise between obtaining a terpolymer with a high molar ratio of allylic to methacrylic pendant $C=C$ bonds and an overall concentration of pendant methacrylic $C=C$ bonds sufficient for detection by ^{13}C -NMR. Methyl methacrylate was included to provide "spacer" units along the polymer chains and to dilute the methacrylic $C=C$ bonds from ethylene dimethacrylate, thereby reducing the probability of grafting and crosslinking of the terpolymer arising during its preparation from reaction of pendant methacrylic $C=C$ bonds which result from polymerization of only one of the $C=C$ bonds in ethylene dimethacrylate. As further measures to prevent extensive grafting of the terpolymer, the polymerization was taken to low conversion (7%) and performed in dilute solution (10%) to eliminate autoacceleration. The low conversion also ensured that polymerization of allylic $C=C$ bonds would be negligible, both in allyl methacrylate and in pendant allylic groups in the terpolymer

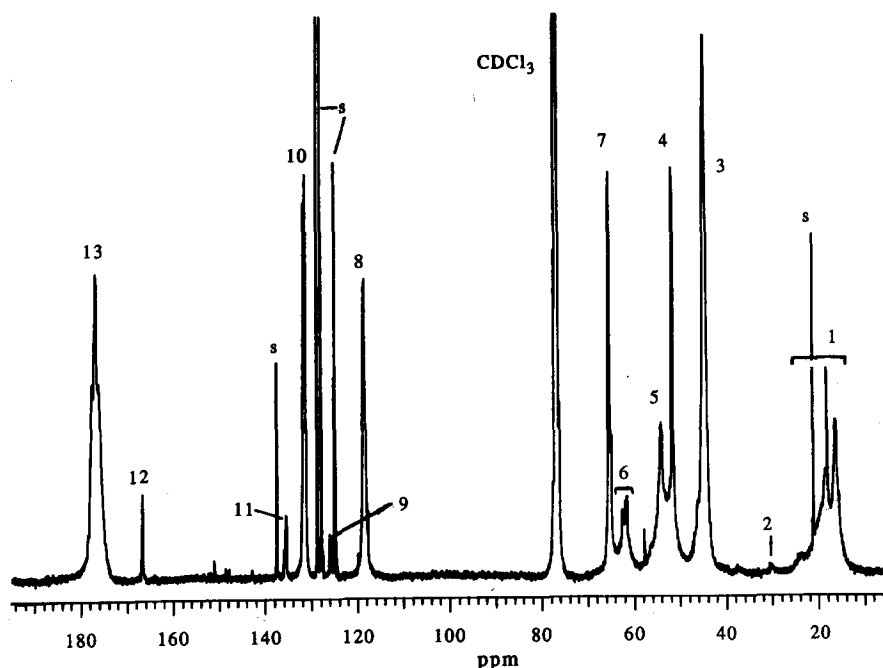


Fig. 9. The ^{13}C -NMR spectrum of the terpolymer prepared from a comonomer mixture comprising allyl methacrylate (50 mol%), methyl methacrylate (40 mol%) and ethylene dimethacrylate (10 mol%). The label s indicates peaks from residual toluene solvent. Peak assignments are given in Table 8.

(which result from polymerization of only the methacrylic $\text{C}=\text{C}$ bond in allyl methacrylate).

The structure of the terpolymer was determined from its NOE-suppressed ^{13}C -NMR spectrum illustrated in Fig. 9 and assigned in Table 8. With respect to methacrylic repeat units, the polymer was found to comprise: 50 mol% allyl methacrylate, 38 mol% methyl methacrylate and 12 mol% ethylene dimethacrylate. The composition, therefore, is in excellent agreement with the feed composition, as expected on the basis that the reactivity of a methacrylic $\text{C}=\text{C}$ bond is independent of the grouping to which it is attached. However, the small signal at *ca* 30 ppm indicates a small amount of polymerization of the pendant allylic $\text{C}=\text{C}$ bonds, correspond-

ing to *ca* 6% of the pendant allyl groups. Additionally, by referencing the integral for the carbonyl carbons in pendant methacrylic groups to that for the carbonyl carbons in methacrylic repeat units, the extent of polymerization of pendant methacrylic $\text{C}=\text{C}$ bonds is found to be *ca* 0.81. Thus the terpolymer contains 47 mol% pendant allylic $\text{C}=\text{C}$ bonds and 2.3 mol% pendant methacrylic $\text{C}=\text{C}$ bonds, giving the relative mole fractions of pendant $\text{C}=\text{C}$ bonds as 0.953 and 0.047 respectively.

In terms of the monomers for which reactivity ratios were measured, the maximum probability for reaction of the pendant allylic groups in the terpolymer would occur for its reaction with *n*-butyl acrylate. However, the ^{13}C -NMR signals from the 2- CH_2 carbon in the side group of *n*-butyl acrylate repeat units (i.e. $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$) [27] would obscure signals at 29–31 ppm from the CH carbons in allyl repeat units and, therefore, prevent detection of the only unambiguous signal identifying polymerization of the allylic $\text{C}=\text{C}$ bonds. Thus, in order to ensure that the 29–31 ppm region would be free from interfering signals, the terpolymer was reacted with ethyl acrylate rather than *n*-butyl acrylate. Literature values of reactivity ratios for copolymerization of ethyl acrylate and *n*-butyl acrylate with a range of different comonomers are very similar and show that it is reasonable to assume the copolymerization behaviour of these two acrylates to be similar [28].

Figure 10 compares the ^{13}C -NMR spectra of the model terpolymer and the products from its reaction with ethyl acrylate. (The spectrum of the product obtained after 4 hr reaction was poorly resolved and so is not included.) It can be seen that the signals from carbon atoms in pendant methacrylate groups diminish as a diagnostic signal from the side group

Table 8. Peak assignments in the ^{13}C -NMR spectrum of the terpolymer of allyl methacrylate, methyl methacrylate and ethylene dimethacrylate (Fig. 9). The monomer units are identified by A, M and E respectively. Polymerized and unpolymerized allylic and methacrylic groups are identified by the notation A_p , A_u , M_p and A_u .

Peak	Chemical shift (ppm)	Assignment
1	16–22	$\alpha\text{-CH}_3$
2	30	A_p backbone CH
3	44–46	M_p backbone C_q
4	52	M OCH_3
5	50–56	M_p backbone CH_2
6	61–63	E OCH_2
7	65.8	A OCH_2
8	119	A_u olefinic CH_2
9	125.5	M_u olefinic CH_2
10	132	A_u olefinic CH
11	136	M_u olefinic C_q
12	167	M_u $\text{C}=\text{O}$
13	175–178	M_p $\text{C}=\text{O}$

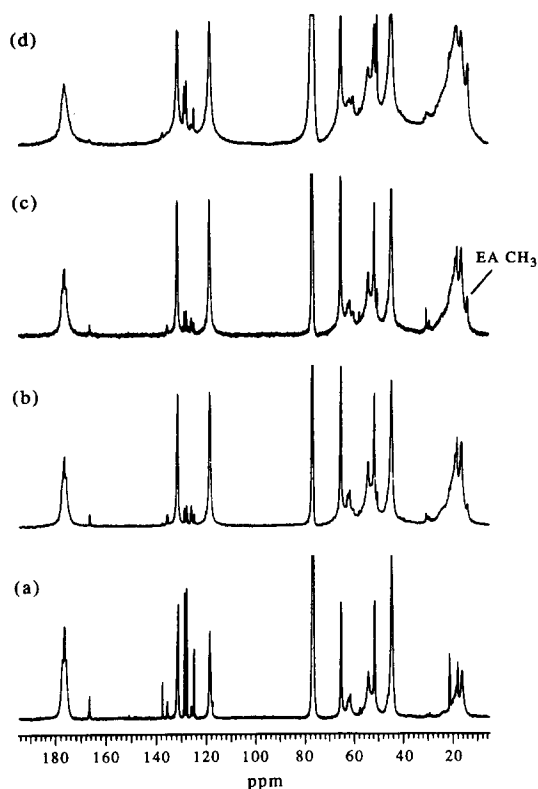


Fig. 10. The ^{13}C -NMR spectra of (a) the terpolymer, and the products from its reaction with ethyl acrylate after reaction times of (b) 1 hr, (c) 2 hr and (d) 6 hr. The signal from CH_3 carbons in ethyl acrylate repeat units is identified in (c). Peaks from residual toluene solvent are present at the chemical shifts indicated in Fig. 9 and partially obscure the CH_2 signal from pendant methacrylic $\text{C}=\text{C}$ bonds.

CH_3 in ethyl acrylate repeat units increases. After 6 hr reaction, only very weak signals from pendant methacrylate groups remain, as is most clearly evident from the very low relative intensities of the characteristic methacrylate C_q and $\text{C}=\text{O}$ signals at 136 and 167 ppm respectively. Over the same period, the signals from the carbon atoms in allylic $\text{C}=\text{C}$ bonds reduce only slightly and there is only a small CH signal from allyl repeat units, showing that the extent of polymerization of the allylic $\text{C}=\text{C}$ bonds is low. Thus, the spectra confirm that it is the pendant methacrylic $\text{C}=\text{C}$ bonds which are consumed in forming poly(ethyl acrylate) grafts on the terpolymer, even though they are present at relatively low concentrations compared to the pendant allylic $\text{C}=\text{C}$ bonds.

CONCLUSIONS

The reactivity ratios measured for copolymerization of allyl acetate with methyl methacrylate, n-butyl acrylate and styrene have confirmed the low tendency towards copolymerization of allylic $\text{C}=\text{C}$ bonds. They indicate that in copolymerizations of allyl methacrylate with (meth)acrylates and styrene, conversion of the allylic $\text{C}=\text{C}$ bonds will only become significant when the extent of reaction of all other types of $\text{C}=\text{C}$ bonds has reached very high values.

The NMR studies of the structure of poly(allyl methacrylate) formed by both bulk and dilute solution polymerization have provided no evidence for the in-chain lactone rings previously reported to result from intramolecular cyclopolymerization of allyl methacrylate [20, 21]. The signals in the NMR spectra of poly(allyl methacrylate) are entirely consistent with "normal" polymerization at the methacrylic and allylic $\text{C}=\text{C}$ bonds.

The theoretical predictions based upon the measured reactivity ratios, when considered together with the observations on the reaction of the model terpolymer, show that the very low concentrations of pendant methacrylic $\text{C}=\text{C}$ bonds, which result from polymerization of the allylic $\text{C}=\text{C}$ bonds in molecules of allyl methacrylate, make a significant contribution to branching and crosslinking.

In the preparation of multi-phase polymers by sequential emulsion polymerization [12–16], particles of a first-phase polymer are formed and then a second-phase polymer is grown onto these particles by addition of a second-stage monomer mixture. Monomers such as allyl methacrylate are used to provide essential graftlinking between the phases. In patents [12–14], it has been suggested that the graftlinking between phases results from copolymerization of second-stage monomer(s) with residual pendant allylic $\text{C}=\text{C}$ bonds produced from polymerization of allyl methacrylate in the first stage. However, it is now clear that the very low concentration of pendant methacrylic $\text{C}=\text{C}$ bonds produced in the first stage may also significantly contribute to graftlinking if they are not completely converted when the second-stage monomer addition is made.

In summary, the results presented in this paper provide a greater understanding, than has previously been available, of the copolymerization behaviour of allyl groups in monomers and of allyl side-groups on polymer chains. Further, quantitative studies of the bulk polymerization of allyl methacrylate and of reactions of model terpolymers are now planned so that theoretical predictions based upon the reactivity ratios reported here can be fully tested against experimental observations.

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