# THE POLYMERIZATION OF ALLYLIC METHACRYLATES PART 1.—ALLYL METHACRYLATE

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The polymerization of dilute (2-12 %) solutions of allyl methacrylate in benzene initiated by benzoyl peroxide or azo-bis-(isobutyronitrile) has been studied. The catalyst exponent is  $\sim 0.5$ , and the monomer exponent rises from  $\sim 1.0$  to  $\sim 1.4$  as the monomer concentration is decreased. Pure allyl methacrylate has been polymerized to give cross-linked polymers. A study of the swelling of these polymers in toluene has enabled values for K, the reactivity of the allyl group relative to that of the methacrylate group, to be deduced. K rises from  $1 \times 10^{-2}$  at 45 % conversion to  $4 \times 10^{-2}$  at 95 % conversion.

Attempts have been made in the past to improve the thermal and mechanical properties of polymethyl methacrylate by the incorporation, during preparation, of small quantities of bifunctional monomers such as ethylene dimethacrylate or allyl methacrylate. Such additions usually produce a harder and stiffer, if somewhat more brittle material. The details of the process are controlled by several factors, notably the relative reactivity of the two groups of the bifunctional mono-This relative reactivity K is the ratio of the rate constants (propagation mer. constants) for the addition of a given type of radical to each of the reactive groups of the bifunctional monomer; hence the value of K will depend on the nature of the reacting radical. However, in some systems, such as mixtures of allyl and methyl methacrylates, where the two monomers have one group in common, and where K is very different from unity, only the value of K characterizing the addition of the more reactive radical will be of importance. Values of K for the polymerization of allyl, and several substituted allyl methacrylates have been determined. These are discussed in parts 1 and 2 of this paper respectively.

The relative reactivity K of two groups is clearly closely related to the reactivity ratio as determined by copolymerization experiments. In general, however, steric effects will tend to reduce the reactivity of a group when pendant from a polymer chain, as compared with that displayed by a free group. For certain monomers such as butadiene, any effect of this nature is obscured by the very large decrease in reactivity consequent upon the loss of conjugation when the first group reacts; such conjugated bifunctional monomers are not considered here. The reduction of reactivity by steric effects has been demonstrated by Smets and Schmets <sup>1</sup> for ethylidene dimethacrylate; here, instead of the expected value for K of unity, a value of 0.7 was observed. Fox and Loeshaek <sup>2</sup> have studied the copolymerization of methyl methacrylate and several glycol dimethacrylates and shown that in some cases only 75 % of the pendent methacrylate groups react.

Recently considerable work on the copolymerization of difunctional and monofunctional monomers has been published by Gordon and his co-workers.<sup>3, 4, 5</sup> Gordon has shown that in certain cases the decrease in reactivity of a pendant vinyl group may be due to other than purely steric effects.

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Certain allyl compounds are known to undergo a polymerization which is terminated by degradative chain transfer. This process, in which transfer occurs with the monomer itself and unreactive allylic radicals are produced, was detected 6 for allyl acetate by a dependence of the rate of polymerization on the first power of the monomer concentration, rather than the more usual one-half power. The kinetics of polymerization of allyl methacrylate do not appear to have been investigated, apart from some work of Cohen et al.,7 which was primarily concerned with defining the conditions necessary to postpone the onset of gelation. Since there is a possibility that this abnormal termination process might be of significance in allyl methacrylate polymerization, a brief survey was made of the kinetics of the process.

#### MATERIALS

## EXPERIMENTAL AND RESULTS

ALLYL METHACRYLATE.—Allyl methacrylate was prepared by direct esterification. A mixture of allyl alcohol (0.5 mole) and methacrylic acid (1.5 mole) was cooled in ice, and sulphuric acid (0.2 mole) slowly added. The mixture was then heated with stirring at  $65^{\circ}$ C for 8 h. After the addition of hydroquinone, the ester was steam-distilled off, washed with 5 % caustic soda, and dried over calcium sulphate. Further hydroquinone was then added and the crude ester vacuum fractionated under nitrogen through a 45 cm helix-packed column to give a main fraction, b.p. 42-44°C/16-17 mm. This was again fractionated and finally distilled into a high-vacuum apparatus, where, after degassing, it was stored at  $-80^{\circ}$ C.

This allyl methacrylate had  $n_{D}^{20}$  1.4366 (lit.<sup>8</sup>, 9 1.4358, 1.4370), and the densities recorded in table 1.

When filling the apparatus used to prepare polymer discs, a knowledge of the vapour pressure of allyl methacrylate was required. Approximate values at a series of temperatures were obtained using a simple mercury manometer immersed in a thermostat, the pressure difference being read off with a travelling microscope. The results are plotted in fig. 1.



FIG. 1.-Variation of vapour pressure of allyl methacrylate with temperature.

BENZENE.—A.R. benzene was dried over calcium chloride, refluxed for several hours over sodium, and finally redistilled from fresh sodium. The product was stored in vacuo at - 80°C.

INITIATORS.—Azo-bis(isobutyronitrile) (AZBN) was recrystallized from toluene and dried in vacuo. Benzoyl peroxide was partially precipitated from chloroform by methanol and dried in vacuo. Both initiators were stored at 0°C.

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TOLUENE.—The toluene used for swelling measurements was a reagent grade product, dried over calcium chloride, and redistilled.

#### PROCEDURE FOR RATE MEASUREMENTS

Both the polymerization of the pure monomer and that of dilute solutions (2-12 %) in benzene were followed dilatometrically. For the pure monomer, dilatometers with 2 ml capacity bulbs and 1 mm precision bore capillaries were used, whilst for the benzene solutions these sizes were increased to 8 ml and 2 mm respectively. After weighing in the required quantity of initiator, a dilatometer was sealed to the vacuum line and the monomer and solvent (if any) distilled in from graduated reservoirs; the dilatometer was then sealed off. The dilatometer was immersed in a thermostat and the movement of the meniscus followed with a travelling microscope reading to  $\pm$  0.01 mm. The polymer could be recovered from a benzene solution of an ungelled reaction product by precipitation with methanol and hence values of the contraction factor were obtained (table 1).

#### RATE OF POLYMERIZATION OF ALLYL METHACRYLATE

In all cases after a short period of acceleration, the rate of polymerization became constant and remained so up to 8-9 % conversion, after which gelation ensued and the meniscus shape was destroyed. Table 2 records the rates of polymerization at constant AZBN concentration over the temperature range  $30-50^{\circ}$ C.

TABLE 1.—DENSITY AND CONTRACTION ON           POLYMERIZATION OF ALLYL METHACRYLATE			TABLE 2.—THE RATE OF POLYMERIZATION			
			OF PURE ALLYL METHACRYLATE INITIATED			
emn °C density g/ml		contraction,	by $9.8 \times 10^{-3}$ M AZBN			
emp: e	density, 5/111	ml/g	temp °C	rate of polymerization		
20	0.934	0.228	temp. C	$g/ml \min \times 10^5$		
30	0.923	0.240	30.0	9.4		
40	0.914	0.253	30.0	9.1		
50	0.903	0.268	39.9	25.0		
60	0.893	0.283	49.6	66.3		
			49.6	70.1		

The overall energy of activation is 20 kcal/mole, which is of the expected magnitude for an AZBN-initiated polymerization.

#### RATE OF POLYMERIZATION OF ALLYL METHACRYLATE IN BENZENE

Rates of polymerization at 55°C of dilute (2-12 %) solutions of the monomer in benzene were measured to determine the dependence of rate upon monomer concentration, and also to avoid complications due to gelation. Rates over less than 5 % reaction were measured. In all cases these rates were constant and no induction period was detected. Rates conveniently expressed as cm/ml min may be converted to mole/l. sec by multiplication by 0.0151.

Log-log plots obtained by varying the monomer and benzoyl peroxide concentrations are given in fig. 2 and 3. These plots show that

#### rate $\propto$ [monomer]<sup>x</sup>[Bz<sub>2</sub>O<sub>2</sub>]<sup>0.42</sup>,

where the value of x rises steadily from  $\sim 1.1$  at the highest monomer concentration to  $\sim 1.5$  at the lowest. As such behaviour is not commonly observed in polymerizing systems, similar measurements were made using AZBN as the initiator. This is known to be less prone to undergo side-reactions and generally to act as a more efficient initiator than benzoyl peroxide. A similar effect was observed (fig. 4), the exponent rising from  $\sim 1.0$  to  $\sim 1.3$  over the same range of monomer concentration (about 2-12 % = 0.13-0.84 M).

## THE PREPARATION AND SWELLING OF GELLED POLYMERS

(a) PREPARATION OF POLYMERS.—The apparatus depicted in fig. 5 was used to prepare thin discs pf polymer suitable for swelling measurements. The glass tray A containing the initiator (0.6 % benzoyl peroxide) was placed in the main apparatus, which was then evacuated via the joint X. The bulb B was cooled in liquid nitrogen and the required quantity of monomer distilled in; allowance was made for the monomer which would

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subsequently be present in the vapour phase. Finally, in order to avoid the monomer distilling out of the tray during polymerization, the apparatus was filled to a pressure of about 500 mm with oxygen-free nitrogen. The polymerization was effected by melting the monomer in B and then, by rotating the bulb about the joint C, transferring it to the tray A; the whole apparatus was then placed in the thermostat at  $55^{\circ}$ C for the required



FIG. 2.-Dependence of rate of polymerization of benzene solutions of allyl methacrylate upon benzoyl peroxide concentration; [allyl methacrylate] = 0.337 M.



FIG. 3.-Dependence of rate of polymerization on allyl methacrylate concentration;  $[Bz_2O_2] = 3.46 \times 10^{-2} \text{ M}.$ 

time. The polymer discs so obtained were weighed, soaked overnight in cold toluene, extracted with boiling toluene for 6 h, and finally heated in a vacuum oven at 40-50°C for 15 h. This cycle was repeated until the polymer had attained constant weight; three cycles were usually adequate. From the weight of gel obtained the degree of gelation of the original reaction product was deduced. In almost all cases very little soluble polymer was present, the reaction product consisting almost entirely of gel plus unreacted monomer.

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(b) SWELLING OF POLYMERS.—Weighed pieces of polymer were placed in coarse sintered-glass crucibles and allowed to swell in toluene held in a large vessel thermostatted at 30°C. The degree of swelling was determined by quickly drying the polymer with hard filter paper, and weighing in a closed vessel. Except for very highly crosslinked polymers, swelling equilibrium was attained in less than 48 h.



By varying the reaction time, a series of polymerized products was obtained containing different proportions of gel. The results of swelling the extracted gel fractions in toluene are plotted in fig. 6.

The gel fraction was isolated from the polymer mass under conditions which would not normally be expected to induce the polymerization of allyl groups, and it was established that the extraction procedure did not lead to any further cross-linking of the polymer.



 TABLE 3.—EFFECT OF THE EXTRACTION

 PROCEDURE ON THE DEGREE OF SWELLING

	swelling ratio			
% insoluble gel	initial	after further extraction		
45.7	4.63	4.69		
	4.64	4.70		
75.3	1.72	1.64		
100	1.66	1.72		

FIG. 5.—Apparatus for the preparation of polymer discs.

Swelling measurements were carried out on two samples of polymer of different degrees of cross-linking, both before and after a further extraction cycle. The results recorded in table 3 show that the degree of cross-linking is unaffected, within experimental error, by the extraction procedure.

#### DISCUSSION

#### DISCUSSION OF RATE MEASUREMENTS

The observed catalyst exponent of 0.42 is close to 0.5 so it may be assumed that a mutual termination process predominates and that any radicals produced by transfer with allyl groups are sufficiently reactive to initiate polymerization through methacrylate groups. This is in accordance with the failure of other workers to detect any retardation of methacrylate polymerization by allylic compounds. In particular, it has been shown <sup>10</sup> that radicals from the allylic hydrocarbon dihydromyrcene, whilst sufficiently reactive to initiate a methacrylate polymerization, fail to initiate the polymerization of vinyl acetate.



FIG. 6.—Swelling of gelled allyl methacrylate in toluene.

There has been considerable controversy with regard to the order of reaction with respect to monomer concentration for polymerization in monomer + solvent systems, though some of the differences appear to be the result of attempts to compare results obtained over different monomer concentration ranges. Variations of monomer exponent with monomer concentration have been observed for a few systems, particularly in aromatic solvents and at low monomer concentrations. For the system methyl methacrylate + benzene the reaction is first order for higher monomer concentrations but even at 20 % there is a trend to a higher order.

This problem has been studied recently by Burnett and Loan,<sup>11</sup> whose results for the methyl methacrylate + benzene system are very similar to those described Burnett and Loan 11 explain their results by postulating that the solvent here. radicals produced by chain transfer processes are not only capable of reinitiating the kinetic chain, but also of reacting with polymer radicals, and further, of undergoing mutual termination. On this basis they derive an expression which indicates that the monomer exponent should rise from 1.0 to 2.0 as the monomer concentration is decreased. The results described above might also be explained in terms of this theory. It must be noted that Burnett and Loan's kinetic analysis requires that all radicals formed during propagation are also predominantly removed by propagation reactions, that is, that all radicals re-initiate rather than terminate. The exponent of catalyst concentration of approximately 0.5 indicates that this limitation is acceptable in the present case.

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#### DISCUSSION OF SWELLING MEASUREMENTS

The equation relating the mean molecular weight  $M_c$  between cross-links and the volume fraction  $v_2$  of polymer in the swollen gel derived by Flory and Rehner <sup>12</sup> and later modified by Flory,<sup>13</sup> is

$$\overline{M}_{c} = -\frac{\rho V_{1}(v_{2}^{1} - \frac{1}{2}v_{2})[1 - (2M_{c}/M/)]}{\ln(1 - v_{2}) + v_{2} + \chi v_{2}^{2}},$$
(1)

where  $V_1$  is the solvent molar volume,  $\rho$  the polymer density, X the polymer-solvent interaction parameter, and  $\overline{M}$  the mean molecular weight of the chains produced by severing all the cross-links. If  $2\overline{M}_c \ll \overline{M}$ , the last term in the numerator of eqn. (1) may be neglected, otherwise the evaluation of  $\overline{M}_c$  from experimental values of  $v_2$ , requires a knowledge of  $\overline{M}$ .

The polymerization of pure methyl methacrylate yields a polymer having a molecular weight of the order of several hundred thousand and  $\overline{M}$  for the polymerization of allyl methacrylate may probably be assigned a similar value. In this connection it may be noted that the polymers prepared by the polymerization of 5 % solutions of allyl and methyl methacrylate in benzene have very similar limiting viscosity numbers. It seems reasonable therefore to assume  $2\overline{M}_c \ll \overline{M}$  for all but the most slightly cross-linked polymers.

No value for X for the polyallyl methacrylate + toluene system at 30°C has been reported. However, Smets and Schmets<sup>1</sup> have evaluated X for polymethyl methacrylate in benzene at 25°C. As an approximation, in view of the similarity of the systems and the small temperature difference, their value of 0.458 has been adopted here.

Values of the weight swelling ratio read off from the smoothed plot of fig. 6 have been converted to  $v_2$  values using the known polymer and solvent densities and assuming no volume change on mixing; from these  $v_2$  values,  $\overline{M_c}$  has been deduced using eqn. (1). These data are given in table 4.

TABLE 4.—VALUES	OF TH	IE MOLECULAR	WEIGHT	$\overline{M}_c$	BETWEEN	CROSS	LINKS	AND
		THE RELATIVE	REACTIV	ITY	K			

olvent/polymer weight swelling ratio	% gelation α	$v_2$	$\overline{M}_{c}$	$\overline{DP}_{c}$	K
0.9	96.3	0.4436	1,320	10.5	3·95 × 10−2
1.0	92.5	0.4180	1,580	12.6	4.41
1.1	88.7	0.3949	1,890	15.0	4.57
1.2	85.3	0.3742	2,240	17.8	4.53
1.3	83.1	0.3558	2,620	20.8	4.23
1.4	80.6	0.3390	3,000	23.8	4.05
1.5	<b>79</b> ·0	0.3236	3,440	27.3	3.74
1.6	76.5	0.3097	3,880	30.8	3.65
1.7	75.1	0.2967	4,490	35.6	3.30
1.85	72.4	0.2795	5,190	41.1	3.14
2.0	70.6	0.2643	6,060	<b>48</b> ·0	2.84
2.25	67.0	0.2419	7,940	6 <b>3</b> ·0	2.44
2.5	64.3	0.2231	9,620	76·4	2.20
2.75	61.3	0.2070	11,800	<b>93</b> .8	1.96
3.0	59.0	0.1932	13,400	106.6	1.85
3.25	56.3	0.1810	17,400	138.0	1.54
3.5	53.8	0.1702	20,000	159.0	1.49
3.75	51.5	0.1607	22,800	181-0	1.38
4.0	<b>49</b> ·1	0.1522	25,500	202.5	1.34
4.25	<b>47</b> ∙0	0.1445	28,600	228.0	1.25
4.2	45.0	0.1376	31,800	252.0	1.20

## POLYMERIZATION OF ALLYL METHACRYLATE

By considering the relative rates of polymerization and of the formation of cross-links, Smets has shown that at a degree  $\alpha$  of monomer to polymer conversion

$$\frac{1}{\overline{DP}_c} = \frac{1}{\alpha} \left\{ \frac{(1-\alpha)^K + \alpha K - 1}{K-1} \right\},\tag{2}$$

where  $\overline{DP_c}$  is the mean degree of polymerization between cross-links and K is the relative reactivity, defined by

$$K = \frac{\text{rate constant for the cross-linking reaction}}{\text{rate constant for chain propagation}} = \frac{k_1}{k_2}.$$

For allyl methacrylate, where the allyl radical is relatively very unreactive, this may be written,

$$K = \frac{\text{rate constant for radical addition to the allyl group}}{\text{rate constant for radical addition to the methacrylate group}} = \frac{k_1}{k_2}$$

Expression (2) is only applicable if no soluble polymer is formed, so that the degree  $\alpha$  of conversion is equal to the degree of gelation. As indicated above, this appears to be true in the present case, certainly for  $\alpha > 40$  %, and only these data have been included in table 4. The values of K derived by the application of eqn. (2) are included in the last column of this table.

The low value of K reflects the relative lack of reactivity of the allyl group; the absolute magnitude  $(1 - 4 \times 10^{-2})$  is comparable with those obtained for the reactivity ratio by copolymerization studies. These values range from  $\sim 4 \times 10^{-2}$  for the allyl acetate + methyl methacrylate system to  $\sim 2 \times 10^{-2}$  for the allyl chloride or chloroacetate + methyl methacrylate systems.<sup>14</sup>

Increasing conversion favours the cross-linking reaction, as is shown by the steady rise in the value of K. K is equal to the ratio of  $k_1$  to  $k_2$  both of which are propagation rate constants, and as such, would be expected to decrease with increasing conversion, though such changes are not generally considered to occur before some 70 % conversion. It appears therefore that steric factors act so as to reduce  $k_2$  rather more than  $k_1$ , the net effect being a rise in the relative reactivity of the allyl group. This conclusion is consistent with the greater degree of substitution of the double bond in the methacrylate group as compared with that in the allyl group; this would be expected to lead to enhanced steric hindrance in reactions of the former group as compared with those of the latter.

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<sup>3</sup> Gordon and McMillan, Makromol. Chem., 1957, 23, 188.

- <sup>5</sup> Gordon, Grieveson and McMillan, J. Polymer Sci., 1955, 18, 497.
- <sup>6</sup> Bartlett and Altschul, J. Amer. Chem. Soc., 1945, 67, 812, 816; 1953, 75, 91.
- <sup>7</sup> Cohen, Ostberg, Sparrow and Blout, J. Polymer Sci., 1948, 3, 264.
- <sup>8</sup> Rehburg, Fisher and Smith, J. Amer. Chem. Soc., 1943, 65, 1003.
- <sup>9</sup> Rutovskii and Shur, J. App. Chem. Russ., 1951, 24, 851.
- <sup>10</sup> Allen, Merrett and Scanlan, Trans. Faraday Soc., 1955, 51, 95.
- <sup>11</sup> Burnett and Loan, Trans. Faraday Soc., 1955, 51, 214, 219.
- <sup>12</sup> Flory and Rehner, J. Chem. Physics, 1943, 11, 521.
- <sup>13</sup> Flory, J. Chem. Physics, 1950, 18, 108.
- <sup>14</sup> Alfrey, Bohrer and Mark, *Copolymerization* (Interscience, New York, 1952), pp. 32 et seq.

<sup>&</sup>lt;sup>1</sup> Smets and Schmets, Bull. Soc. Chim. Belg., 1953, 62, 358.

<sup>&</sup>lt;sup>2</sup> Fox and Loeshack, J. Polymer Sci., 1955, 15, 371.

<sup>&</sup>lt;sup>4</sup> Gordon and Roe, J. Polymer Sci., 1956, 21, 27, 39, 57, 75.