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Cross-linked Polymers. I. Factors Influencing the Efficiency of Cross-linking in Copolymers of Methyl Methacrylate and Glycol Dimethacrylates[1]

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A method is presented for determining the residual unsaturations in copolymers of methyl methacrylate with glycol dimethacrylates, and the fraction of dimethacrylate molecules which have reacted at both ends (the cross-linking efficiency) is calculated from the result. Residual unsaturations are determined from a comparison of the observed volume contractions per mole of double bond with the corresponding contractions for complete conversion of monomer to polymer. In the several instances where comparisons were made, the results are shown to be in satisfactory agreement with residual unsaturations determined by infrared analyses. The efficiencies are found to depend markedly on the concentration and structure of the dimethacrylate and are generally less than one. For copolymers containing dimethacrylates of ethylene glycol, decamethylene glycol or 2-ethyl-2-butylpropanediol-1,3, the efficiency is limited by geometrical restrictions on the motions of unsaturated vinyl groups attached to the cross-linked network. An approximate theory is presented for this case which satisfactorily accounts for the observed dependence of the efficiency on the degree of cross-linking and on the length of the cross-linker. For the dimethacrylate of 2,2-dimethylpropanediol the efficiency is limited by the occurrence of glass formation in the polymerizing system. Only a qualitative interpretation of the data was possible in this case. It is indicated that high efficiency in a cross-linking reaction may be obtained by employing (1) a divinyl molecule with a very long flexible chain between vinyl groups and (2) a polymerization temperature which exceeds the second-order transition temperature of the cross-linked product.

Introduction

In the copolymerization of a difunctional with a monofunctional vinyl compound it has long been suspected that the number of cross-linkages produced is not equivalent to the number of difunctional molecules employed. However, no quantitative study has been published on the efficiency of the cross-linking reaction, *i.e.*, on the fraction of the divinyl monomer which reacts at both ends. In the present work a simple method is presented for determining the residual unsaturation in cross-linked copolymers of methyl methacrylate with glycol dimethacrylates and for calculation of the efficiency of cross-linking from this result.

In calculating the degree of unsaturation in a copolymer from the observed volume change during polymerization it has been assumed that the volume change associated with the addition of a double bond in a vinyl monomer to a growing radical is independent of both the extent of conversion and the structure of the monomer. Evidence in support of the first assumption has been given for methyl methacrylate (MMA)[2] and other vinyl monomers.[3,4] The validity of the second assumption is demonstrated by the approximate constancy of the molar volume contraction for a number of methacrylates as determined by Crawford[5] and as calculated from the density data of Nichols and Flowers.[6] This is further substantiated in the present investigation by the agreement for homopolymers of MMA and of various glycol dimethacrylates between the values for the residual unsaturation obtained by the volume contraction method and by infrared analyses.

Data will be given over the whole composition range for the efficiency of cross-linking of MMA with the dimethacrylates of: ethylene glycol (EGDMA), decamethylene glycol (DGDMA), 2,2-dimethylpropanediol-1,3 (2-2-D-PDMA) and 2-ethyl-2-butylpropanediol-1,3 (2-E-2-B-PDMA). The factors affecting the efficiencies will be discussed and an equation will be given relating the efficiency to the concentration and chain length of the cross-linker.

Experimental

Glycol Dimethacrylates.—The difunctional monomers were prepared by direct esterification of the required glycol in benzene solution with a 25% excess of methacrylic acid and about 1% of sulfuric acid as a catalyst. They were purified by distillation under reduced pressure with the addition of 2–3% by weight of the relatively non-volatile inhibitor 1,1′-bi-2-naphthol (di-β-naphthol).

From the analytical data in Table I it is evident that complete conversion of the glycol to the corresponding dimethacrylate did not always result. Statistical considerations show that the fraction of the glycol unreacted at both ends is negligible at high degrees of esterification. Therefore, it will be assumed that any unreacted hydroxyl group is part of a half esterified glycol molecule. *The glycol dimethacrylate preparations containing the "half ester" will be designated as "cross-linker mixture."* Mole fractions of half ester (m_h) in the cross-linker mixtures calculated from the saponification numbers on the basis of the above assumption are given in the last column of Table I. The mole fraction of dimethacrylate, m_d, in a copolymer mixture containing the mole fraction, m_m, of cross-linker mixture and mole fraction $m_{MMA} = 1 - m_m$ of MMA is given by the equation.

TABLE I

Monomer[a]	B.p. °C.	B.p. mm.	Mol. wt. Observed (M_m)[b]	Mol. wt. Theoretical (M_d)	Mole fraction half ester (m_h)
EGDMA	58	0.18	198	198	0
DGDMA	124	.07	307	310	0.046
2-E-2-B-PDMA	104	.15	291	296	.082
2-2-D-PDMA	100	2.0	230	240	.150

[a] Acid number = 0 for all monomers. [b] Calcd. from the observed saponification numbers.

$$m_d = (1 - m_h)m_m \qquad (1)$$

The weight fraction of cross-linker mixture, w_m, is

$$w_m = \frac{m_d M_m/(1 - m_h)}{m_m M_m + m_{MMA} M_{MMA}} \qquad (2)$$

where $M_{MMA} = 100$ is the molecular weight of MMA and M_m is the molecular weight of the cross-linker mixture (column 4 of Table I).

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[1] Presented before the Division of High Polymer Chemistry at the Atlantic City Meeting of the American Chemical Society, September 16, 1952.

[2] G. V. Schulz and G. Harborth, *Angew. Chem.*, **A59**, 90 (1947).

[3] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

[4] H. W. Melville and L. Valentine, *Proc. Roy. Soc. (London)*, **A200**, 337 (1950).

[5] J. W. C. Crawford, *J. Soc. Chem. Ind.*, **68**, 201 (1949).

[6] F. S. Nichols and R. G. Flowers, *Ind. Eng. Chem.*, **42**, 292 (1950).

Methyl Methacrylate (MMA).—Commercial monomer (Rohm and Haas), was washed successively with aqueous solutions of sodium nitrite, sodium bisulfite and sodium hydroxide. After two washings with water, it was dried over Drierite and distilled under reduced pressure (100 mm.) in a stream of dry nitrogen with about 2–3% of di-β-naphthol as an inhibitor. The middle fraction boiling at 46° was retained.

Polymerization of Samples.—Two-gram samples of the required mixtures of MMA and cross-linker containing 0.1% by weight of benzoyl peroxide were polymerized by heating successively for various periods at 60, 125 and 150°. The polymerizations at 60° were carried out in sealed evacuated 10-mm. Pyrex ampoules which were immersed in an oil-bath until polymerization was apparently complete. In several instances most of the monomer would polymerize in about 20 hours, but a very thin unreacted layer always remained at the top, and occasionally an additional two or three days were required for this thin layer to react. In no case did this layer amount to more than *ca.* 2–3% of the sample. Subsequently the polymers were heated for about 130 hours in air in an oven at 125°, and then for 5 or 6 hours in evacuated ampoules at 150°.

Samples for infrared analyses were prepared by casting the monomer between glass plates to give sheets about 0.01 cm. thick. These polymerizations were carried out for about 20 hours at 60° and then for about 24 hours at 125°.

Densities.—Density data were obtained at 30° on the monomer mixtures before the addition of the initiator. The measurements were made with a 1-ml. pycnometer with a precision of ±0.1%. Similar determinations on the pure monomer with a 5-ml. pycnometer were precise to ±0.01%.

Density measurements were made at room temperature by the water displacement method on 1- to 2-g. samples of the copolymers after the heat treatments at each of the three polymerization temperatures. Weighings were made to ±0.1 mg. Room temperature densities were converted to 30° with the available coefficients of volume expansion.[7] The density measurements on the copolymers were generally made with a precision of ±0.25%. A slightly larger uncertainty (*ca.* 0.5%) was obtained at 150° since in this case the samples sometimes contained numerous small fissures. The corresponding uncertainties in the fractional conversions calculated below are ±0.01 to ±0.02 unit.

Infrared Analyses.—A Perkin-Elmer 12-B spectrophotometer with NaCl optics was operated at constant slit. Transmitted energy curves were recorded over the carbon-carbon double bond stretching region for monomer specimens of accurately known path length in fixed absorption cells, and for solid films of 0.10–0.15 mm. (micrometered) thickness and sufficient area to cover the entrance slit of the spectrometer. The recorded data were handled by base line absorbance methods in order to minimize atmospheric water vapor and ester carbonyl stretching interference. Complete absence of conjugated olefin links for a base line absorbance cell constant reference was represented by the similarly recorded transmitted energy curve of ethyl propionate.

All of the monomeric methacrylates examined were found to peak strongly and sharply in absorption at 6.10 ± 0.01 μ due to conjugation of the olefin link with the ester carbonyl group. When expressed in terms of absorbance per unit path length per weight per cent. methacrylate functional group ($CH_2{=}C(CH_3)C{=}O$), the monomer absorptivities were found to be approximately constant. Consequently, the determination of small amounts of residual monomers in the partially polymerized systems was carried out by a straightforward application of the law of optical absorption by means of an average absorptivity per methacrylate group.

Results

Molar Volume Contractions for Methacrylates.—Evidence in support of the assumption that the volume contraction associated with the polymerization of a mole of double bonds is nearly the same for methacrylates of similar structures is given in Table II. Values of the molar contractions at 20° given by Crawford[5] are higher than the corresponding values at 25° calculated from the data compiled by Nichols and Flowers,[6] contrary to expectations. This discrepancy, which is as much as 4 cc./mole, indicates the magnitude of the experimental errors. Within this limit, it may be concluded that the molar contraction for the various methacrylates (and two acrylates) are similar, *i.e.*, about 22 to 23 cc./mole. This is consistent with the postulate[8] that the polymerization of a vinyl monomer involves the exchange of a double bond and a van der Waals bond for two covalent bonds.

TABLE II

MOLAR VOLUME CONTRACTIONS FOR VINYL MONOMERS

Monomer	ΔV (cc./mole) Calcd. from data of ref. 6 (25°)	ΔV (cc./mole) Data of ref. 5 (20°)
Methyl methacrylate	22.6	21.9
Ethyl methacrylate	22.3	23.0
n-Propyl methacrylate	21.3	24.2
n-Butyl methacrylate	22.7	24.7
Isobutyl methacrylate	20.6	24.4
Neopentyl methacrylate	..	20.6
Methyl acrylate	22.6	..
Ethyl acrylate	21.0	..

Apparent molar volume contractions (Table III) were calculated in the present case for MMA and for each of the difunctional monomers from density data at 30° on the monomers and polymers. For MMA the result, 23.0 cc./mole, agrees with the data in Table II. For the difunctional monomer the contractions are much lower, indicating that not all of the double bonds in these monomers have reacted. The conversions which have been attained, calculated on the assumption of 23.0 cc. per mole of double bonds for complete polymerization, are given in the fourth column of Table III. The agreement between these figures and values obtained from infrared absorption data on the corresponding polymer films (last column) is within the experimental accuracy, thus supporting the assumption that the molar volume contraction is essentially the same (23.0 cc./mole at 30°) for each of these monomers.

TABLE III

EXTENT OF POLYMERIZATION AT 125° BY VOLUME CONTRACTION AND BY INFRARED ANALYSIS

Monomer	Contraction cc./g., 30°	Apparent ΔV, cc./mole	% reacted (100 ΔV)/23.0	% reacted obtd. by infrared
MMA	0.230	23.0	100	99-100
EGDMA	.149	14.8	64	Some unsaturation[a] remains
DGDMA	.155	19.8	86	80
2-2-D-PDMA	.124	15.4	67	No data
2-E-2-B-PDMA	.114	17.3	75	70

[a] A sample of suitable dimensions for a quantitative determination could not be obtained with this polymer because of its tendency to crack.

Specific Volume of Monomer and Copolymer.—The specific volumes of the monomer mixtures measured at 30° are presented in Fig. 1 as a function of the weight fraction (w_m) of cross-linker mixture. The data in each case are fitted by a smooth curve. Departures from linearity are small except for the MMA–DGDMA monomer mixtures.

Densities obtained at 30° for the copolymer after the 125° heat treatment are presented in Fig. 2. The data in each case are fitted by a smooth curve. Similar curves were obtained after the heat treatments at 60° and at 150°.

Efficiency of Cross-linking.—The fractions, p, of all of the vinyl groups which have reacted in the four copolymer systems after heat treatment at 60, 125 and 150° are given in Fig. 3. These were calculated from density data such as given in Figs. 1 and 2 by the equation

$$p = (\bar{v}_m - \bar{v}_p)/23.0\, N_{db} \quad (3)$$

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[7] S. Loshaek, *Phys. Rev.*, **86**, 652 (1952). These results will be published in more complete form in the second paper of this series.

[8] A. V. Tobolsky, F. Leonard and G. P. Roeser, *J. Polymer Sci.*, **3**, 604 (1948).

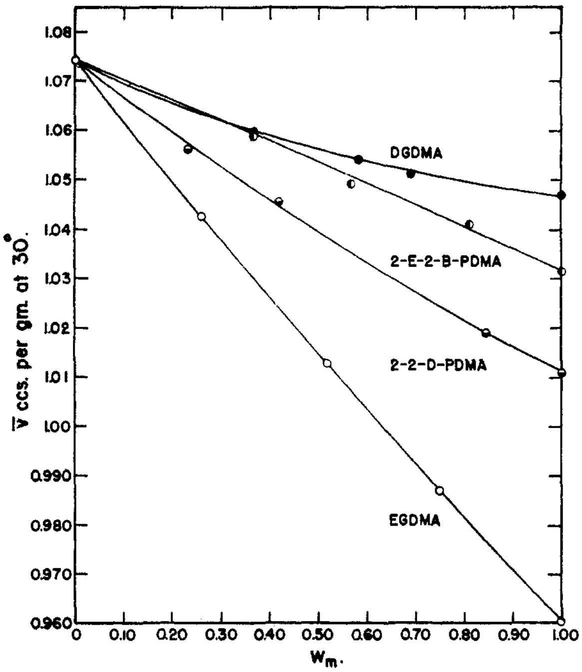

Fig. 1.—Specific volume ($\bar{v}$) of the comonomers plotted against weight fraction of "cross-linker mixture" (w_m).

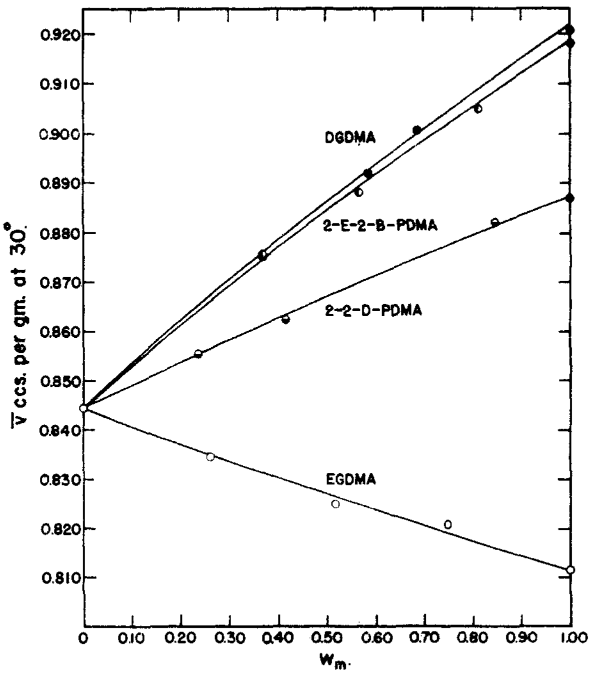

Fig. 2.—Specific volume ($\bar{v}$) of the copolymers after polymerization at 125°, plotted against weight fraction of "cross-linker mixture" (w_m).

where $\bar{v}_m$ and $\bar{v}_p$ are the specific volumes at 30° of the monomer mixture and the corresponding copolymer, respectively, and N_{db} is the number of moles of double bonds in a gram of monomer mixture, *i.e.*

$$N_{db} = \frac{m_{MMA} + m_b m_m + 2m_d}{m_m M_m + m_{MMA} M_{MMA}} \tag{4}$$

Smooth curves were drawn through the points obtained at the highest temperature of cure, 150°, with the assumption that $p = 1$ for pure MMA. Within the experimental error of 0.01 to 0.02, the value of p is essentially independent of temperature from 60 to 150° for DGDMA, 2-E-2-B-PDMA and EGDMA copolymers , while for 2-2-D-PDMA the conversion increases with increasing temperature. Except for the 2-2-D-PDMA copolymers, the 150° curves are believed to represent the maximum conversions which may be obtained.

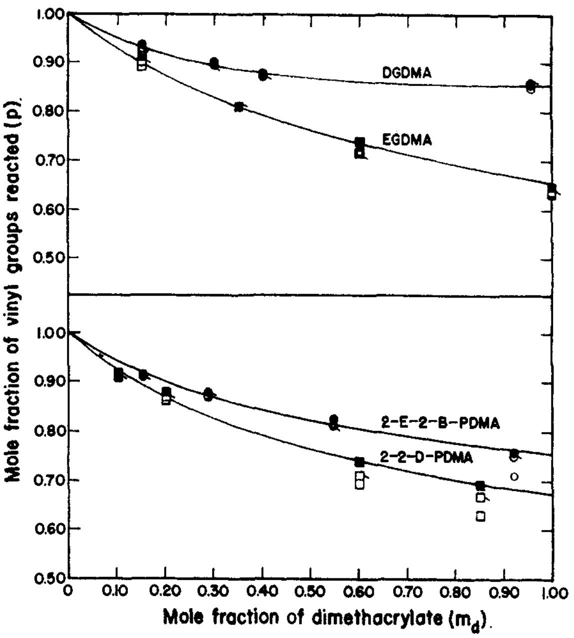

Fig. 3.—The effect of polymerization temperature (T_p) on the mole fraction of vinyl groups reacted (p) for copolymers containing different mole fractions of dimethacrylate monomers (m_d): ○ or □, T_p = 60°; ○̗ or □̗, T_p = 125°; ● or ■, T_p = 150°.

Since little loss in weight occurred when thin samples of copolymers of this type were heated under vacuum (*ca.* 10^{-6} mm.) at 180° for periods up to an hour, it is concluded that substantially all of the monofunctional components

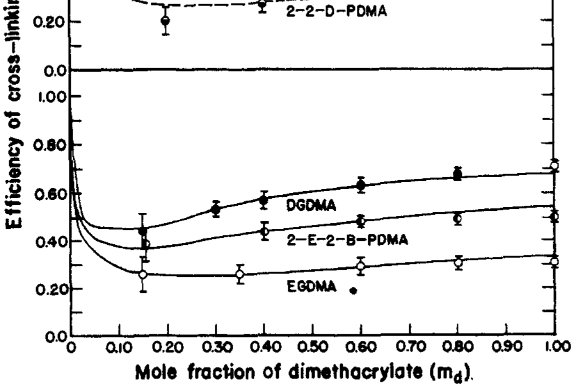

Fig. 4.—Efficiency of cross-linking (ϵ) plotted against the mole fraction of dimethacrylate monomer in the copolymer (m_d). The circles indicate values of ϵ calculated from the experimental data by eqs. (5) and (6). The solid curves represent values of ϵ calculated by eqs. (10) and (11) with the parameters of Table IV. The dashed curve indicates that ϵ is limited by the glass transition temperature in this case.

(MMA plus glycol half ester) have reacted and all of the divinyl monomers have reacted at least once. It follows that the fraction p_x of cross-linker functional groups which have reacted may be calculated from the relationship

$$p_x = \frac{p(m_{\mathrm{MMA}} + 2m_d + m_h m_m) - (m_{\mathrm{MMA}} + m_h m_m)}{2m_d} \quad (5)$$

Furthermore, the number N_s of moles of dimethacrylate molecules reacted at only one end for a gram of mixture originally containing N_d moles of difunctional monomer per gram will be $2N_d(1 - p_x)$. The efficiency of cross-linking ϵ, *i.e.*, the fraction of the difunctional monomer reacted at both ends, is therefore

$$\epsilon = (N_d - N_s)/N_d = 2p_x - 1 \quad (6)$$

Values of ϵ calculated for the various copolymers by equations (5) and (6) from values of p taken from the smooth curves in Fig. 3 are represented by the points in Fig. 4. The lengths of the vertical lines drawn through the points of Fig. 4 represent the magnitudes of the uncertainties in ϵ, assuming in each case an uncertainty of ± 0.01 in p. Since the uncertainty in ϵ becomes very large at low concentrations of cross-linker, values of ϵ have not been calculated for m_d values less than 0.10 or 0.15.

From the points in Fig. 4 it is evident that the efficiency of cross-linking in these copolymerizations is generally less than 1.0 and varies with the concentration and structure of the cross-linker. Unfortunately, the data do not define the behavior precisely at low concentrations of cross-linker ($m_d < 0.15$) but it is believed that the efficiency will approach 1.0 as m_d approaches zero. The solid curves presented in Fig. 4 were calculated by a semi-empirical equation which will be discussed below.

Discussion

Relative Reactivity Ratios.—On the basis of electronic and steric considerations, Alfrey, *et al.*,[9] have classified difunctional monomers of the type employed in the present investigation as having two groups of equal reactivity, the reactivity of a given group being independent of whether or not the first group is reacted. Structural considerations also suggest that their reactivity is not likely to differ appreciably from that of MMA. Nevertheless, the reactivity of the vinyl group which is already attached at one end to the cross-linked network is less than that of the others, since a number of these unreacted pendant groups are left at the end of the reaction. We must look, then, for causes for the lowered reactivity of a methacrylate group attached to a cross-linked polymer network.

Factors Limiting the Conversion of Pendant Vinyl Groups.—Previous workers have indicated that the rate constants for the termination[10-12] and the propagation[12] reactions in a free radical polymerization will decrease as a result of the decrease in diffusion rate of chain radicals with increasing conversion of monomer to polymer. In the present case, the diffusion rate of a pendant unreacted vinyl group will be lowered since its motions must be coördinated with those of other segments of the network. Consequently, the mobile monomer will polymerize more rapidly than the pendant vinyl groups and the last stages of the copolymerization will involve free radicals and vinyl groups attached to the polymer network.

The restrictions on the diffusibility of the pendant vinyl groups may be sufficient not only to lower their reactivity ratios but also to *prevent* their reaction. Obviously, a collision between an unreacted vinyl group and a radical is required for reaction. Such collisions will occur infrequently when the diffusion rate of the reactants becomes very low, *e.g.*, if the polymerizing system reaches its glassy state during polymerization,[13] or not at all if the distances between unreacted vinyl groups on the network polymer become too great. The first effect will be important if the polymerization temperature (T_p) is below the glass transition temperature (T_g) for the completely polymerized system. In such cases (*cf.* 2-2-D-PDMA), the cross-linking efficiency should increase with increasing T_p. In the second case, when glass formation does not occur during polymerization (*cf.* DGDMA, 2-E-2-B-PDMA and EGDMA), the limiting conversion will be determined by the geometrical restrictions on the motions of the pendant groups attached to the cross-linked network. Since the restrictions will be insensitive to temperature, the limiting conversion will be independent of T_p. An approximate calculation of the geometrical factors influencing the efficiency of cross-linking will be given in the next section.

Geometrical Restrictions on the Efficiency of Cross-linking.—At the limiting conversion, cross-linked copolymers polymerized above their glass transition temperatures have been shown above to contain a number of unreacted vinyl groups on the ends of singly reacted divinyl chains. It is believed that these pendant groups fail to react because the volume elements or domains in which neighboring groups are to be found do not overlap. The volume or domain available to a particular group will depend on the magnitude of the thermal motions of both the pendant chain and the portion of the network to which it is attached. The average size of this domain will then be related to the number n_s of chain atoms in the pendant cross-linker side chain, and to the average number n_c of chain atoms between cross-linkage points. In the following treatment we shall simplify the problem by replacing the actual domain by an equal number of equivalent spheres each of the same radius R. At low conversions there is a substantial overlapping of these spheres, but as the reaction proceeds the overlapping decreases until at the limiting conversion no two spheres touch. It will be assumed that *at this limiting conversion the fraction f of the total volume actually occupied by the spheres is the same for all cross-linked copolymers*, thus making it possible to calculate values of R from the experimental data. In view of the simplicity of the model, the absolute values of the radii will not be significant and we shall be interested only in how the relative values depend on n_s and n_c. A semi-empirical relationship between R and the parameters n_s and n_c will then be established. This will be used to interpret the efficiency curves obtained in this study, and to predict the cross-linking efficiencies which should obtain for cross-linkers other than those employed here.

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[9] T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization" (High Polymers Series Vol. 8), Interscience Publishers, Inc., New York, N. Y., 1952, Chapter IX.

[10] E. Trommsdorff, P. B. Report No. 23, 816 (BIOS 363); *cf.* also E. Trommsdorff, H. Köhle and P. Lagally, *Makrom. Chem.*, **3**, 169 (1948).

[11] G. V. Schulz and G. Harborth, *ibid.*, **1**, 106 (1947).

[12] M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).

[13] T. Alfrey, G. Goldfinger and H. Mark, *J. Applied Phys.*, **14**, 700 (1943).

In the cross-linked copolymer at the limiting conversion there are N_s moles of unreacted pendant vinyl groups per gram, *i.e.*, in a total volume $\bar{v}$ where $\bar{v}$ is the specific volume of the copolymer. If the volume available to each group is assumed to be that of a sphere of radius R, then the total volume occupied by the unreacted groups is $4/3\ \pi\ R^3\ \mathbf{N}\ N_s$ where **N** is Avogadro's number. It will be further assumed that reaction ceases when

$$4/3\pi R^3 \mathbf{N} N_s = f\bar{v} \qquad (7)$$

where f is a constant for all copolymers. Since the proper value to be used for f is unknown and since we shall not be concerned with the absolute magnitude of R, it is convenient to take $f = 1$. Combining eqs. (6) and (7) and recognizing that $N_d = m_d/(100 + Bm_d)$, where $B = (\mathrm{M}_m - \mathrm{M}_{\mathrm{MMA}})/(1 - m_h)$, we obtain

$$R = (K/N_s)^{1/3} = \left[K\,\frac{100 + Bm_d}{m_d(1 - \epsilon)}\right]^{1/3} \qquad (8)$$

where $K = \ /(4/3\ \pi\ \mathbf{N})$. This equation may be written in the alternate form

$$\epsilon = 1 - K/N_dR^3 = 1 - K\,\frac{(100 + Bm_d)}{m_dR^3} \qquad (8\text{-}1)$$

Values of R calculated by eq. (8) from the data in Fig. 4 for DGDMA, 2-E-2-B-PDMA and EGDMA are plotted against m_d in Fig. 5. In each case R decreases rapidly with increasing concentration of cross-linker from a high value at low m_d toward a limiting value at higher values of m_d. Furthermore, the magnitude of the limiting R is greater the longer the cross-linker.

The nature of the $\epsilon - m_d$ curves in Fig. 4 can now be understood in terms of eq. (8–1) and the curves of Fig. 5. At low m_d the efficiency decreases rapidly with increasing m_d because of the large decrease in R resulting from the restrictions on chain motions caused by the introduction of an increasing number of cross-linkages into the polymer network. At high concentration of cross-linker the magnitudes of the motions of the network elements are small and the volume available to the vinyl group is determined primarily by the length of the pendant cross-linker chain. Hence, in this region the efficiency is essentially constant and is higher the longer the cross-linker employed. The observed increase in ϵ with increasing m_d in this region of essentially constant R follows according to eq. (8–1), from the increase in N_d. Physically this means that at constant R the number (N_s) of pendant groups remaining at the end of the reaction is a constant (eq. 8) irrespective of the value of m_d, hence the *fraction* of groups reacted must increase as the number of moles (N_d) of divinyl monomer introduced is increased.

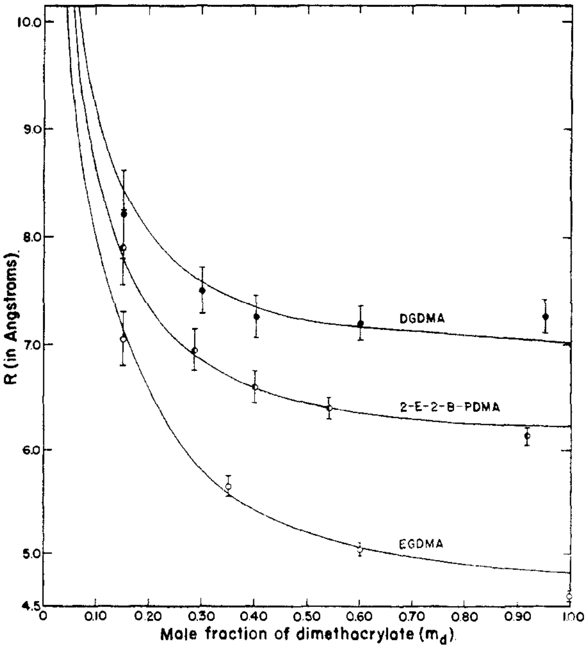

Fig. 5.—Effective lengths (R) in Å. units of the pendant vinyl groups plotted against the mole fraction of dimethacrylate monomer (m_d) in the copolymers. The circles represent values of R calculated from experimental data by means of eq. (8). The curves represent values of R calculated by eqs. (9) and (10) with the parameters of Table IV.

It is now desired to establish a relationship expressing R as a function of n_s and n_c. On the basis of theoretical considerations which will be published at a later date[14] it can be shown that when the ratio n_c/n_s is small, say less than 2, the effective domain averaged over all of the vinyl groups in the system may be represented approximately by an equivalent sphere of radius

$$R = an_c + bn_s^{2/3} \qquad (9)$$

where a and b are constants related to bond distances.[15]

A test of eq. (9) is provided by plotting values of R from Fig. 5 against the corresponding values of n_c calculated by means of the equation

$$n_c = 1 + 1/\epsilon m_d \qquad (10)$$

Although the points are somewhat scattered, they may, in accordance with theory, be represented within the limits of the experimental uncertainty by parallel straight lines whose intercepts at $n_c = 0$ are higher, the higher is n_s. Parallel lines are employed since the slopes are dependent on the structures of the network chains, which are identical for these copolymers. The values of the parameters a and bn_s obtained from the slopes and in-

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(14) S. Gratch and T. G Fox.

(15) In deriving this equation it was assumed that the two cross-linkages at the ends of a network chain are fixed at their most probable average positions, an assumption akin to one made by Flory and Rehner in their treatment of rubber-like elasticity of cross-linked networks.[16] The distance from one of these cross-links to the ith atom in the network chain was assumed to be $r_i \pm \Delta r_i$, where r_i is the most probable value for this separation and Δr_i may vary from zero to an upper value which is proportional to the greatest attainable value of r_i consistent with the requirements of fixed bond distances and valence angles. The analogous assumption was made concerning the end to end distance for a pendant vinyl chain. Inherent in this treatment is the assumption that the number of configurations containing atoms located at distances greater than the maximum value of Δr_i from their most probable positions is too small to result in a measurable rate of reaction between neighboring vinyl groups.

Although different relations could be assumed between Δr_i and r_i, the one used here appears logical on physical grounds and its usefulness is illustrated by the successful application of eq. (9) to the present data.

The assumption that the cross-linkages are in fixed positions becomes increasingly invalid as n_c gets larger, and the statistical and geometrical relationships employed in this calculation will fail at very low values of n_c. Hence, eq. (9) is expected to be in error both for very high and very low values of n_c.

(16) P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 512 (1943).

tercepts, respectively, of the "best" set of parallel lines are presented in Table IV. It is expected that the values of b will be constant for pendant chains of similar structure. Values of b for DGDMA and EGDMA are in agreement, within the uncertainty ($\pm 5\%$) in their determination. The higher value of b obtained for 2-E-2-B-PDMA undoubtedly reflects the steric effects of the bulky side groups in this cross-linker.

TABLE IV

MOLECULAR PARAMETERS FOR DIFUNCTIONAL MONOMERS

Comonomer with MMA	a. Å./atom	$bn_s^{2/3}$, Å.	n_s	b
DGDMA	0.103	6.80	16	1.07
2-E-2-B-PDMA	.103	5.90	9	1.37
EGDMA	.103	4.35	8	1.09

Equations (8–1), (9) and (10) can be combined to give

$$\epsilon = \left[1 - \frac{KB}{(an_c + bn_s^{2/3})^3}\right] \Big/ \left[1 + \frac{100K(n_c - 1)}{(an_c + bn_s^{2/3})^3}\right] \tag{11}$$

which is a form suitable for numerical calculation of ϵ. With the parameters of Table IV this expression was used to calculate ϵ for DGDMA, 2-E-2-B-PDMA and EGDMA for various values of n_c, the corresponding values of m_d being calculated by eq. (10). The results are given by the solid lines in Fig. 4. The good agreement with the data together with the constancy of the parameters a and b discussed above illustrate the usefulness and validity of the equation for the range of concentration covered in the present experiments. A reliable calculation of ϵ cannot be obtained from eq. (11) for values of m_d below 0.05, however, because the assumptions inherent in eq. (9) fail in this region.[15] Even so, the lines drawn in Fig. 4 according to eq. (11) for this low range are probably more reliable than the data which may be obtained in this region *by the present method.*

Examination of eq. (11) shows that high efficiencies may be obtained (1) for any value of n_s at high values of n_c, and (2) only for high values of n_s for low values of n_c. Taking $m_d = 1$ and employing the values of b from Table IV, it is found from eq. (11) that to obtain a cross-linking efficiency of 0.9, the cross-linker must contain a minimum of 40 chain atoms.

In deriving the above relationships it was assumed that the initial reactivity ratios for the polymerization of the first vinyl group of the divinyl monomer (r_2) was equal to or less than the reactivity ratio for the monovinyl monomer (r_1). For systems wherein this assumption is not valid, *e.g.*, $r_2 > 1 > r_1$, the divinyl monomer will be removed preferentially from the monomer mixture. The result is akin to polymerizing fresh monomer in the presence of the cross-linked copolymers obtained in this investigation, *i.e.*, the cross-linking efficiencies will necessarily be greater than those predicted by eq. (11). Copolymers of styrene and divinylbenzene appear to fall in this category.[7,17] In those cases wherein an alternating copolymer is formed, *i.e.*, for $r_1 r_2 \cong 0$, the cross-linking efficiency will also be higher than predicted above if the initial mixture contains an excess of the monovinyl monomer ($m_d < 0.5$).

Limitations on the Efficiency of Cross-linking Resulting from Glass Formation.—The glass transition temperatures of copolymers of MMA with 2-2-D-PDMA show a steady increase in T_g from 105° for MMA to 145° for the copolymer containing 17 mole per cent. of the cross-linker.[7] Above 17 mole per cent. of 2-2-D-PDMA it is probable that the maximum temperature of polymerization ($T_p = 150°$) is below the T_g for the completely polymerized system. For the other copolymer systems the observed glass transition temperatures[7] were 20 to 70° below 150°. It is expected, therefore, that for all of the copolymers polymerized at 60° and for the copolymers containing more than 17 mole per cent. of 2-2-D-PDMA, the upper limit of the efficiency of cross-linking is imposed by the extremely low rate of diffusion for the reactants in the glassy state, and is lower than the limit imposed by the geometrical restrictions considered heretofore.

Evidence for the limitation of conversion of monomer to polymer by glass formation in a linear polymer system is provided by the data of Schulz and Harborth[11] on MMA. Their observation that the conversion of monomer to polymer is dependent on the polymerization temperature can be quantitatively interpreted[18] by assuming that polymerization will proceed until the monomer–polymer mixture is obtained whose T_g is exactly equal to T_p. Similar considerations will hold for cross-linked copolymers except that in this case the glass transition temperature of the incompletely polymerized system will depend not only on the presence of unreacted monomer, but also on the presence of cross-links, and on the chemical composition.

It follows both from the data of Fig. 4 and from a more detailed examination of the above considerations that the ϵ *versus* m_d curve for 2-2-D-PDMA will be qualitatively similar to the curves drawn for the other copolymers. For convenience, therefore, the dotted line (Fig. 4) for this copolymer has been drawn according to eq. (11), with a value of 0.103 for a and 4.75 for $bn_s^{2/3}$. This equation is used in this case merely as an empirical relation of appropriate form, since the theoretical arguments by which it was derived are not applicable here.

Since the observed glass transition temperatures of all of the copolymers studied are greater than 60°, it would be expected that the fractional conversions, p (Fig. 3) would increase when T_p is raised from 60 to 150°. However, in only 8 of 16 cases was an increase in p greater than 0.01 observed. The reason for this insensitivity of p to T_p is not understood.

Conclusion.—Experimental methods employed in this study provide a simple means of measuring unsaturation in vinyl polymers, and indicate that, in general, the efficiency of cross-linking in a monovinyl–divinyl copolymerization will be less than one. In the absence of glass formation, the restrictions imposed by the network structure on the

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(17) H. Staudinger and E. Husemann, *Ber.*, **68B**, 1618 (1935).

(18) T. G Fox, W. B. Shultz and A. R. Schultz, to be published.

motions of the pendant vinyl groups prevent the reaction from going to completion. For cases wherein the activities of the vinyl groups are similar, a theory has been presented by which predictions of the cross-linking efficiency can be made, at least for copolymers containing more than about 5 or 10 mole per cent. of the divinyl monomer. Although the theory in its present preliminary form is based on a simplified model, nevertheless it provides an analytical expression which satisfactorily represents the observed dependence of the efficiency on the degree of cross-linking and on the length of the cross-linker. This is of great practical utility since we are thereby enabled to predict the efficiency curve for copolymers of MMA with the dimethacrylates of similar structure but of different length, *e.g.*, *it was possible in the present case from the observed efficiency curve for EGDMA to predict accurately the curve for DGDMA before any measurements were made on the latter system.* It is expected that the range and systems for which reliable predictions can be made will be extended by future theoretical and experimental work.

In those copolymers wherein the extent of cross-linking is limited by the onset of the glassy state during polymerization, quantitative prediction of the cross-linking efficiency awaits a more detailed knowledge of the factors which determine the temperature at which glass formation occurs.[7]

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Measurement of Ordinary Diffusion Coefficients of Polymers[1]

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Ordinary diffusion coefficients have been measured for several polymers using a method involving diffusion from a porous frit. The validity of the experimental method was checked by comparison with free boundary diffusion measurements on polyvinyl alcohol, dextran, and bovine serum albumin. The diffusion of polyacrylic acid was also investigated in relation to its ionization.

A great variety of physical-chemical measurements have been carried out for the purpose of characterizing polymer molecules in solution. Of the various properties so measured, that of ordinary diffusion has been relatively neglected, mainly because of the difficulty of obtaining accurate values of that quantity. Although the significance of an ordinary diffusion coefficient is evident, its measurement is often unsatisfactory because of the slow rate at which polymer molecules diffuse. Recently, however, a rapid method for measuring diffusion coefficients of substances in solution was described.[2] This method involves saturating a porous disc with the solution to be investigated and then suspending the disc in a large bath of solvent. From a knowledge of the apparent weight of the suspended disc as a function of time, it is possible to deduce the extent of diffusion from the disc and to calculate, by simple graphical means, the ordinary diffusion coefficient of the solute.

The idea of diffusion into a porous material was employed previously by Aten and v. Dreven,[3] but they did not determine the extent of the diffusion by weighing a suspended disc. The present authors have recently learned, however, that Schulze[4] used the change in buoyant force technique nearly 40 years ago to follow movement out of a frit, although he was not concerned with high molecular weight substances.

The purpose of the present paper is to report results obtained by the frit method for some polymers in solution. Some of the results are also compared with data obtained by an optical method with generally good agreement.

Experimental

The apparatus and technique employed were the same as previously described[2] except that the solvent container was placed in a large constant temperature bath. In addition, solvent was kept covered to prevent cooling by evaporation; this precaution was particularly important when volatile organic solvents were employed.

Porous plates which had been soaked with polymer solution were suspended in the bath of solvent from one arm of an analytical balance, and the apparent weight was measured as a function of time. If W is the absolute value of the difference between the apparent weights at time t and after a long (infinite) time, then the asymptotic slope of the line obtained by plotting log W *vs.* t is proportional to the diffusion coefficient. A characteristic frit constant, K, is determined by calibration so that the diffusion coefficient D can be obtained from the aforementioned slope by the simple relationship

$$D = -K \times \text{slope}$$

Values of the frit constants were determined by carrying out diffusion experiments on aqueous potassium chloride solutions. Using the value 2.91×10^{-5} cm.^{2}/sec. for the diffusion coefficient of 0.1 N HCl[5] at 25°, frit no. 1 (see Table I) was found to have a characteristic constant equal to 17×10^{-4}. Further experiments using 0.5 N KCl for

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(2) F. T. Wall, P. F. Grieger and C. W. Childers, THIS JOURNAL, **74**, 3562 (1952).

(3) A. H. W. Aten, Jr. and J. v. Dreven, *Trans. Faraday Soc.*, **44**, 202 (1948).

(4) G. Schulze, *Z. physik. Chem.*, **89**, 168 (1914).

(5) W. A. James, E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **7**, 89 (1939).