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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Elias, Hans-Georg(1983) 'Molar Masses in Multifunctional Addition Polymerizations', Journal of Macromolecular Science, Part A, 19: 2, 239 – 251

To link to this Article: DOI: 10.1080/00222338308069438

URL: <http://dx.doi.org/10.1080/00222338308069438>

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Molar Masses in Multifunctional Addition Polymerizations

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ABSTRACT

The dependence of mass average molar masses, M_w , on monomer conversion, u , in multifunctional addition polymerizations can be described by the semiempirical relationship

$$\log M_w = \log M_w^0 + Ku$$

where M_w^0 is the corresponding molar mass of the primary molecules. According to tests with various literature data, this equation holds for relative monomer conversions u/u_{gel} up to 0.7-0.8, where u_{gel} is the conversion at the gel point.

The addition polymerization of multifunctional monomers has been investigated experimentally and theoretically by many authors. Most papers seem to be interested in a comparison of experimentally observed gel points with theoretical predictions. Relatively few publications, on the other hand, deal with the variation of molar masses with monomer conversion during the course of polymerization. In no case could the conversion dependence of molar masses be described by present theoretical approaches.

In this paper a semiempirical equation is proposed for the conversion dependence of molar masses. The equation is valid up to fairly high monomer conversions relative to the gel point as shown by tests with literature data.

GENERAL CONSIDERATIONS

The addition polymerization of multifunctional monomers proceeds in general in three stages: formation of linear ("primary") macromolecules with pendent functional groups, branching through these groups and, finally, intermolecular cross-linking leading to gelation, i.e., the occurrence of macromolecules of "infinite" molar mass [1]. In addition, intramolecular cyclization reactions may occur which, in special cases, lead to cyclopolymerizations and the absence of gelation [2]. Differences of opinion exist as to the relative extent of the three stages, the importance of intramolecular reactions, and the applicability of the various theories to the different polymerization stages, such as the classical statistical theories [3-5], the cascade theory [6, 7], the percolation theory [8-10], and various kinetic approaches [11, 12].

Simple kinetic considerations show that primary molecules are already formed at very low monomer conversions. Free radical polymerizations reach their steady-state conditions for radical concentrations of approximately 10^{-8} mol/L. If the molar mass of the primary molecules is 10^5 g/mol and if the steady state is exclusively controlled by polymer radicals (which is approximately true for low initiator concentrations), then the steady state is reached for polymer concentrations of 10^{-3} g/L, i.e., at very low monomer conversions.

The pendent groups of primary molecules must be already subject to further reactions at these very low monomer conversions, regardless of whether all groups are equally accessible or only a fraction thereof, e.g., the groups on the periphery of the primary macromolecules. Pendent functional groups may be attacked by primary polymer radicals (or by initiator radicals if the initiator concentration is high) and the thus formed branched polymer radicals may add further monomer molecules. The higher the mass ("weight") average molar mass, M_w , of a primary molecule, the greater the likelihood of a radical attack. The increase of mass average molar mass with fractional degree of conversion, u , must therefore be proportional to the mass average molar mass, or

$$dM_w/du = K'M_w \quad (1)$$

or, after integration, with $M_w \rightarrow M_w^0$ for $u \rightarrow 0$, and after introduction of decadic logarithms,

$$\log M_w = \log M_w^0 + Ku \quad (2)$$

where M_w^0 is the mass average molar mass of the primary molecules. Equations (1) and (2) refer to the increase of molar masses with conversion of monomer, i.e., intermolecular reactions only. Intramolecular reactions reduce the number of pendent functional groups available for intermolecular reactions and thus the proportionality constant, K , but these do not change the interrelationship between M_w and u .

Equation (2) should thus hold over a fairly large range of reduced fractional monomer conversion, $u_{\text{red}} = u/u_{\text{gel}}$, where u_{gel} is the fractional monomer conversion at the gel point. Since branching alone does not lead to gelation [3], addition of polymer radicals onto primary polymer molecules and recombination of branched polymer radicals are the two ways to achieve gelation. Other termination steps, such as the disproportionation reaction of polymer radicals or the termination by initiator radicals, neither increase the degree of polymerization nor the probability for intermolecular polymer/polymer reactions. An exception may be intermolecular chain transfer to primary or branched molecules since the newly formed polymer radicals may add further monomer molecules which in turn increases the molar mass. The probability of such transfer reactions is, however, small compared to addition of polymer radicals to primary or branched molecules. The greater the proportion of the other termination reactions relative to recombination, the greater should be the conversion range over which Eq. (2) should be valid.

RESULTS

Equation (2) was tested with literature data for the dependence of molar masses of various polymers on monomer conversion. A good linear relationship between $\log M_w$ and u was found at low conversions for the thermal polymerization of 1,4-divinylbenzene (DVB) in benzene solutions (Fig. 1). No independence of molar mass on conversion for the beginning of the reaction, as claimed by the authors [13], is visible in this plot. Rather, the polymerization data for the two initial DVB concentrations at 70°C scatter around the same straight line as one would expect for such small differences in initial monomer concentrations. Furthermore, the polymerizations at 70 and 55°C give the same mass average molar mass for the primary molecules although the slope coefficients are different (Table 1).

Similar good correlations were observed for three of the five sets of data on 1,4-divinylbenzene/styrene copolymerizations by Soper et al. [12] (Fig. 2). The other two sets show nonsystematic deviations at higher monomer conversions which may be caused by experimental error.

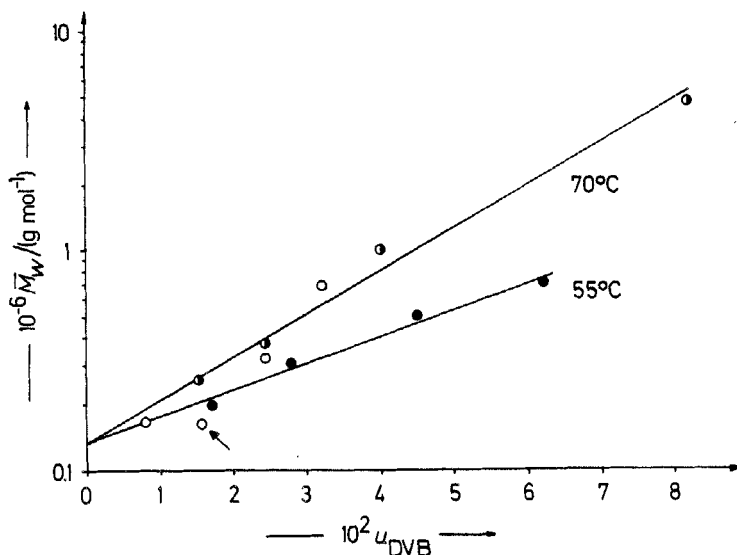


FIG. 1. Logarithms of mass average molar masses of 1,4-divinyl benzene polymers as function of monomer conversion (data of Kast and Funke [13]). Initial monomer concentrations: 0.57 (○) and 0.67 (●) mol/L at 70°C and 0.53 mol/L (●) at 55°C. The data point indicated with an arrow was not used for the calculations.

Plots for the data on diallyl phthalate are shown in Fig. 3. The data of Ito et al. [14] almost certainly contain a systematic error since the molar masses were obtained by gel permeation chromatography (GPC) and not by absolute methods. GPC determines molar volumes which in turn depend on branching. This fact may be partly responsible for the relatively low correlation coefficients, especially for the number-average molar mass data, since the correlation coefficient is much higher for the corresponding data of Simpson et al. [15] (Table 1). The data of Matsumoto et al. [16] were also obtained by gel permeation chromatography. Since they were given as number-average molar masses and show little change with increasing conversion, they were not subjected to correlation analysis.

Mass average molar mass/conversion data were also reported for ethylene dimethacrylate [17], albeit for fractional vinyl group conversions, β , and not for fractional monomer conversions, u . Despite the unknown change of vinyl group content of polymers with monomer conversion, very good correlations between $\log \bar{M}_w$ and β were obtained for the data reported in Table 2 of the paper of Galina et al. [17] (see also Table 1).

TABLE 1. Primary Mass Average Molar Masses, M_w^0 , Slope Coefficients, K , and Correlation Coefficients, C , for the Polymerization of 1,4-Divinylbenzene (DVB), Diallyl Phthalate (DAP), and Ethylene Dimethacrylate (EGMA) as a Function of Initial Monomer Concentration $[M]_0$, Type of Solvent, Polymerization Temperature, and Maximum Reduced Monomer Conversion, $u_{red}^{max} = u_{red}^{max}/u_{gel}$

Multifunctional monomer		Solvent	Polymerization temperature in °C	u_{red}^{max}	$10^{-3} M_w^0$ g/mol	K	C	Ref.
Name	$[M]_0$ mol/L							
DVB	0.67; 0.57	Benzene	70	?	132^{+24}_{-21}	19 ± 1.2	0.9812	13
DVB	0.53	Benzene	55	?	133^{+12}_{-11}	12 ± 1.1	0.9824	13
DVB	0.0385	1.335 mol/L (styrene + DVB) in toluene	95	?	374 ± 8.4	8.5 ± 0.18	0.9991	12
DVB	0.0096		95	?	400 ± 18	5.0 ± 0.36	0.9898	12
DVB	0.0048		95	?	415 ± 2.0	2.65 ± 0.047	0.9996	12
DAP	Bulk	-	60	0.78	10 ± 1.0	2.6 ± 0.22	0.9521	14
DAP	Bulk	-	60	0.78	6.7 ± 0.30^a	0.6 ± 0.18	0.6910	14
DAP	Bulk	-	80	0.89	2.3 ± 0.30^a	3.49 ± 0.047	0.9998	15
EGMA	3.75	Benzene	50	0.78^b	1586 ± 0	23.7 ± 0	0.9999	16
EGMA	2.5	Benzene	50	0.78^b	830 ± 38	16 ± 1.4	0.9926	16

^aNumber average.
by vinyl group conversion.

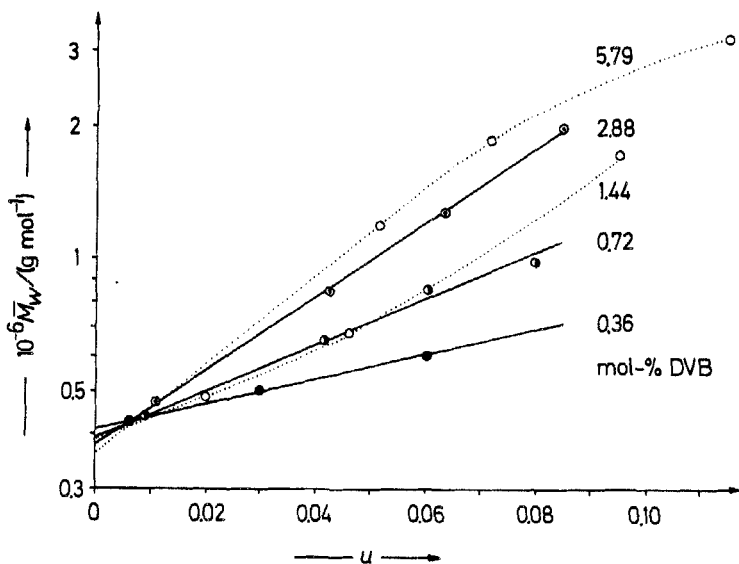


FIG. 2. Logarithms of mass average molar masses of 1,4-divinyl benzene/styrene copolymers as function of monomer conversion. The numbers give the initial DVB concentrations in terms of total monomer content. Data for 5.79 and 1.44 mol% DVB (open circles and dotted lines) were not used for calculations. Data were taken from Fig. 5 of Soper et al. [12].

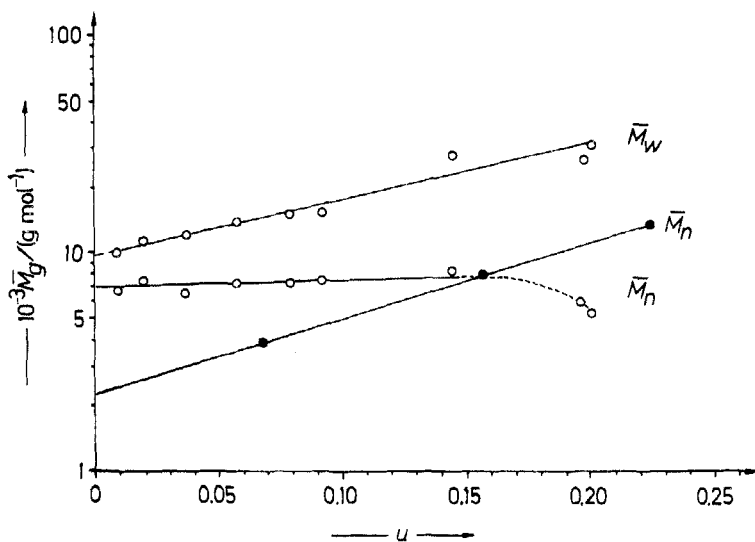


FIG. 3. Logarithms of molar masses of diallyl phthalate as function of monomer conversion. (\circ) Data of Ito et al. [14]; (\bullet) of Simpson et al. [15].

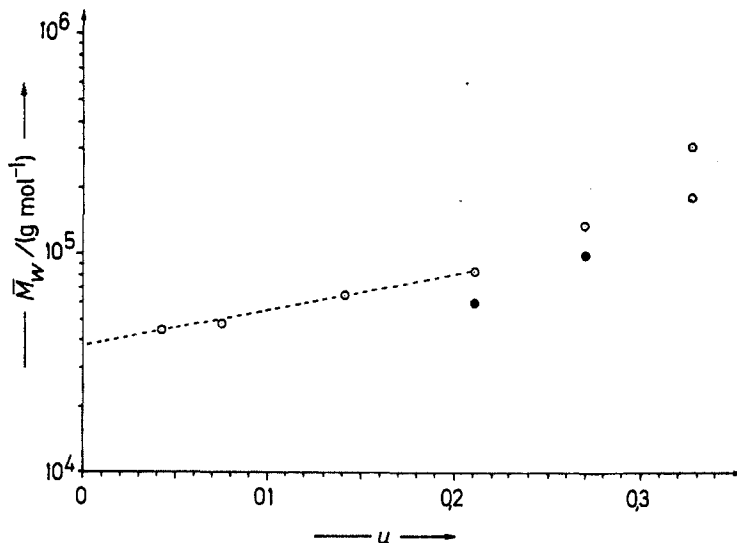


FIG. 4. Logarithms of mass average molar masses as function of monomer conversion in the polymerization of styrene with 1 mol% DBV in benzene solution [18]. (○) GPC, (●) light scattering.

The data of Okasha et al. [18] on styrene/DVB polymerizations in benzene showed upward deviations from the linear $\log M_w = f(u)$ plot at relatively low conversions (Fig. 4). These polymerizations were, however, carried out with very small amounts of DVB (1 mol% with respect to styrene) and furthermore in very dilute solution and in the presence of chain transfer agents. Under these conditions, the likelihood of a radical attack on the primary macromolecules is small at low conversions but increases dramatically at higher conversions. These data and those of Fink [19] on the polymerization of styrene with 0.3-1.2 mol% divinyl compounds were thus not further considered since they represent very special cases of such multifunctional polymerizations.

Dilution reduces the probability of intermolecular additions relative to intramolecular reactions according to the Ruggli-Ziegler dilution principle. The ratio, $K/(\log M_w^0) = K^{int}$, should thus be a normalized measure for intermolecular additions since the slope coefficient K itself is a measure of intermolecular additions of polymer radicals to primary macromolecules. The intrinsic slope coefficient should decrease with increasing dilution of the multifunctional monomer and must pass through the origin at infinite dilution. Such a linear relationship between K^{int} and the initial monomer concentration was indeed found for ethylene dimethacrylate

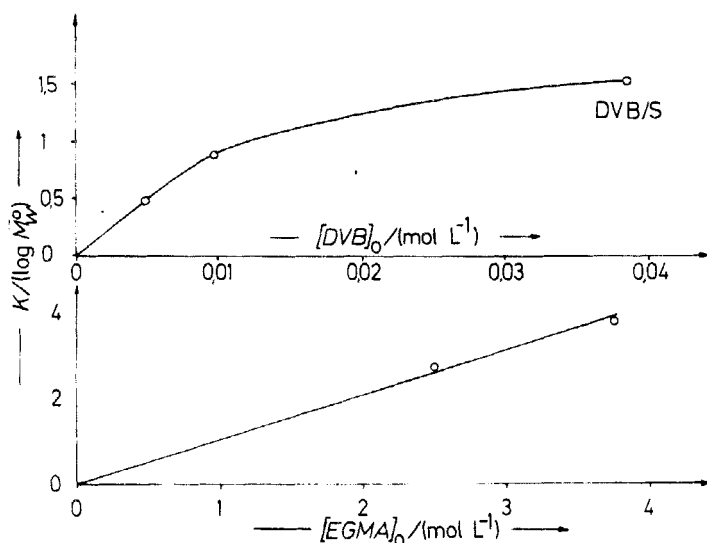


FIG. 5. Variation of the intrinsic slope coefficient $K/(\log M_w^0)$ with initial concentration of multifunctional monomer for ethylene dimethacrylate and 1,4-divinyl benzene/styrene. Data from Table 1.

polymerizations (Fig. 5). Deviations from this linearity exist for the DVB/styrene system, however, which may be caused by the simultaneous variation of both the initial divinylbenzene and styrene concentrations by the authors [12] who kept constant the total concentration of the two monomers.

DISCUSSION

The predicted linear relationship between the logarithms of mass average molar mass and monomer conversion is well observed for all multifunctional polymerizations reported in the literature for relative monomer conversions smaller than 78-89%. Correlation coefficients generally range between 0.9812 and 0.9999. The two lower correlation coefficients (0.9521 and 0.6910) were obtained for GPC data which are inappropriate for polymers with systematic changes in molecular branching.

No systematic deviations from Eq. (2) were observed up to reduced fractional monomer conversions of $u_{red} = 0.78-0.89$. Any avalanche effect leading to infinite molar masses at the gel point must therefore occur at reduced fractional monomer conversions higher than

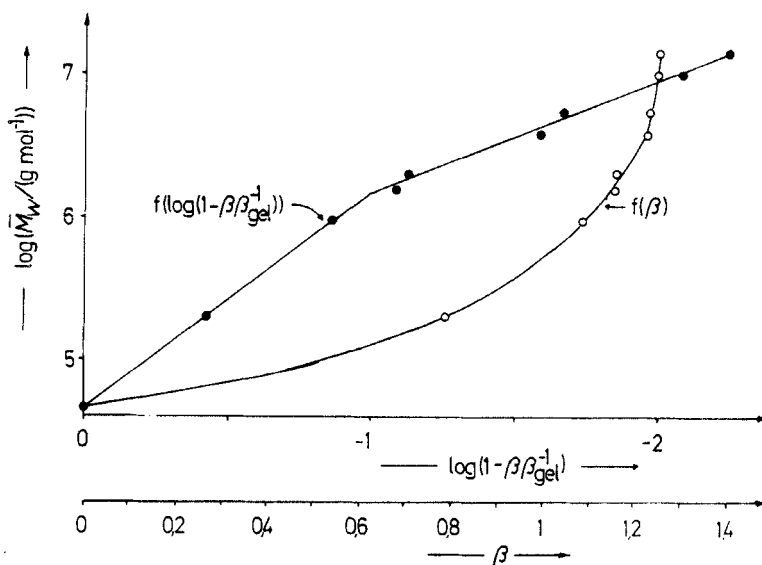


FIG. 6. Logarithm of mass average molar masses of ethylene dimethacrylate/methyl methacrylate copolymers as function of vinyl group conversion β (\circ) or the logarithm of $(1 - \beta\beta_{\text{gel}}^{-1})$ (\bullet). Data of Whitney and Burchard [20].

0.8-0.9 as shown by the data of Whitney and Burchard [20] for copolymers of ethylene dimethacrylate and methyl methacrylate (Fig. 6), albeit for reduced fractional conversions of functional groups, $\beta/\beta_{\text{gel}} > 0.63$. These authors did not measure mass average molar masses below this high relative vinyl group conversion so that Eq. (2) could not be tested for their data. Furthermore, their data [20] as well as those of others [17] refer to vinyl group conversions, β , and not to monomer conversions, u , which may introduce another uncertainty. Although both conversions are interrelated via the fractional residual unsaturation, γ ,

$$\beta = u(1 - \gamma) \quad (3)$$

data can often not be interconverted since residual unsaturations have not always been determined for all monomer conversions and vice versa. Extrapolation of data obtained at the gel point to lower relative monomer conversions may not be helpful since the residual unsaturation of, e.g., diallyl phthalate may change with monomer conversion [14] although it was found to be constant by other authors for

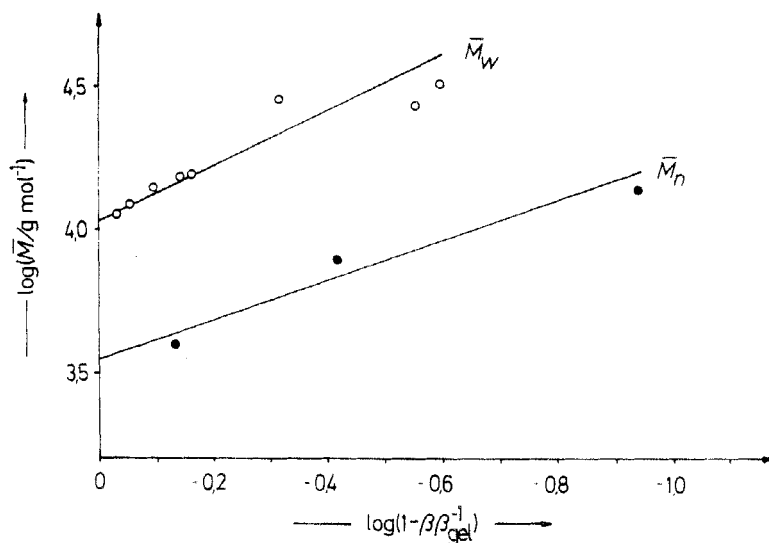


FIG. 7. Test of percolation theory with data on diallyl phthalates. Data of Ito et al. [14] (\circ ; \bar{M}_w) and Simpson et al. [15] (\bullet ; \bar{M}_n).

the same monomer [15] and also for 1,4-divinylbenzene [13]. The decrease of residual unsaturation with conversion should increase with either high initial initiator concentrations or low initial monomer concentrations. In the former case, initiator radicals may add onto functional groups; in the latter, intramolecular reactions may be dominant.

The good semiempirical correlation between $\log \bar{M}_w$ on one hand and u or β , respectively, on the other, does of course not exclude other correlations. Percolation theory [8-10] predicts, e.g.,

$$\bar{M}_w = \bar{M}_w^0 (1 - \beta\beta_{gel}^{-1})^{-\nu} \quad (4)$$

or

$$\log \bar{M}_w = \log \bar{M}_w^0 - \nu \log (1 - \beta\beta_{gel}^{-1}) \quad (5)$$

where β is the functional group conversion, β_{gel} the corresponding conversion at the gel point, and ν a constant with a values of 1.8. Only the data on diallyl phthalate [14, 15] could be used to check Eq. (5) since only here were gel points and residual unsaturations determined in addition to molar masses and monomer conversions

TABLE 2. Mass Average Molar Masses of Primary Molecules, M_w^0 , Slope Coefficients, ν , and Correlation Coefficients, C, Evaluated from Literature Data for Bulk Polymerized Monomers Using Eq. (4)

Monomer	β_{red}	$\frac{10^{-3} M_w^0}{g/mol}$	ν	C	Ref.
DAP	0-0.78	$11^{+1.8}_{-1.6}$	0.60 ± 0.086	0.8901	14
DAP	0-0.88	$3.6^{+0.85}_{-0.69} a$	0.64 ± 0.16	0.9428	15
EGMA/MMA	0-0.9	44.8 ± 0.34	1.528 ± 0.0054	0.99999	17
EGMA/MMA	0.9-0.994	227^{+23}_{-21}	0.80 ± 0.040	0.9900	17

^aNumber average.

(Fig. 7). The evaluation of the data with the help of Eq. (5) resulted in much lower correlation coefficients, however (see Table 2). The slope coefficients ν are also far lower than the theoretically predicted values of 1.8. It could be argued that this might be expected since Eq. (5) was derived for molar masses near the gel point (i.e., $\beta_{\text{red}} > 0.9$) and the data apply to values of $\beta_{\text{red}} < 0.78-0.88$. However, the data on ethylene glycol dimethacrylate/methyl methacrylate copolymers [20] seem to indicate two straight lines (which seems to have escaped the notice of the authors) with a higher slope coefficient for the lower reduced group conversions, albeit with high correlation coefficients for both conversion regions. The transition between the two regions corresponds to reduced group conversions $\beta_{\text{red}} \sim 0.9$ which may explain why such a behavior was not found for the polymerization data of Table 1. Clearly, more experiments in both the high and low molar mass regions, with low and very high monomer conversions, and with additional determination of residual unsaturations are needed to solve the problem of molar mass dependence on monomer or group conversion in multifunctional polymerizations.

ACKNOWLEDGMENT

The author appreciates the help of Mr Kevin Battjes with the computer calculations.

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Accepted by editor April 5, 1982

Received for publication May 3, 1982