The Determination of Reactive-Group Functionality from Gel Point Measurements*

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Synopsis

The usual method of calculating functionality is to divide the molecular weight by the equivalent weight. Because of the uncertainty of molecular weight determinations in the range 1000–20,000 a more precise method is needed. Several authors have published work concerning the determination of the extent of reaction at the gel point through the functionalities of the reactants. It occurred to us that this method could be reversed. We chose Stockmayer's treatment, with some changes, to calculate the average functionality of carboxyl-terminated polybutadiene (CTPB): $(P_A P_B)_{gel} = (f_E - 1)^{-1}(g_E - 1)^{-1}$, where f_E and g_E are the weighted average functionalities of all molecules bearing the reactive groups A and B, and P_A and P_B are the fractions of initially present groups that have reacted. Two systems with an epoxide and glycerol as curing agents were investigated. The influence of dilution was investigated. Nonfunctional polybutadiene did not interfere with the accuracy of the determination of carboxyl functionality. By changing the ratio of epoxide to COOH groups from 0.6 to 1.4 it was shown that the calculated functionality remained constant. Weight-average molecular weights for three CTPB samples were calculated from the functionality and the equivalent weight. They were compared with those obtained from intrinsic-viscosity measurements. The precision of the functionality numbers is believed to be ±1%.

INTRODUCTION

Prepolymer technology is a relatively new science in which polymer structures of any desired type are built from partially polymerized resins containing reactive functional groups. Well over one hundred low molecular weight polymers and crosslinking agents are currently available commercially. Since the physical properties of polymer networks depend on the crosslink density, and the crosslink density is largely determined by the prepolymer's reactive-group equivalent weight and the average number of reactive groups per molecule (functionality), the functionality is of greatest importance to those working with these materials. Functionality is usually calculated by dividing molecular weight by equivalent weight. The determination of molecular weight in the range 1000–10,000 is, however, subject to an uncertainty of at least ±5%, even when one is sure that he is working with a pure material. A need exists for a more precise method.

DISCUSSION

The manufacturers of alkyd resins for coatings have had a related problem. They need to know the gel point of their mixture fairly precisely, so that they can stop the "cook" short of the gel point. They have been able to do this by using equations connecting the extent of reaction at the gel point with the functionality of the reactants. These equations were developed by Flory,[1] Stockmayer,[2] Carothers,[3] and others.[4-10]

It occurred to us that this method could be reversed and the functionality calculated from the extent of reaction at the gel point. In order to do this, the equation connecting the various factors must be in terms of two average functionalities, one for each type of reactant, each functionality capable of taking on any positive value. Flory limited his theory to systems in which only one of the reactants had a functionality greater than 2, whereas Stockmayer extended the theory of three-dimensional condensation polymers to reactions between molecules with two different functional groups but no restricted functionality distribution. The original mixture of monomers consists, therefore, of A_1, A_2, A_3, ... A_i moles of reactants, bearing respectively f_1, f_2, f_3, ..., f_i functional groups of type A, and of B_1, B_2, B_3, ..., B_j moles with functionalities g_1, g_2, g_3, ..., g_j of type B.

Assuming that a carboxyl-containing prepolymer has a distribution not only in the molecular weight but also in the functionalities of its carboxyl groups, we chose Stockmayer's treatment[2c,d] to calculate the average functionality of carboxyl-terminated polybutadiene (CTPB) according to the equation

$$(P_A P_B)_{gel} = (f_E - 1)^{-1}(g_E - 1)^{-1} \tag{1}$$

where P_A and P_B are the fractions of A and B groups initially present that have reacted at the gel point, and

$$f_E = (\Sigma_i f_i{}^2 \times A_i)/(\Sigma_i f_i \times A_i) \tag{2}$$

$$g_E = (\Sigma_j g_j{}^2 \times B_j)/(\Sigma_j g_j \times B_j) \tag{3}$$

The f_E and g_E are the weighted average functionalities of all molecules, bearing the reactive groups A or B, respectively. The A groups (e.g., carboxyl groups) can react only with B groups (e.g., hydroxyl groups), and vice versa. At every time of reaction equal amounts of reactive groups of types A and B must have reacted.

By transformation of eq. (1) one can write

$$P_A P_B = P_A{}^2/r = P_B{}^2 r = 1/(f_E - 1)(g_E - 1) \tag{4}$$

$$f_E = 1 + r/P_A{}^2(g_E - 1) = 1 + 1/rP_B{}^2(g_E - 1) \tag{5}$$

where r is the ratio of the total number of B groups initially present to the total number of A groups initially present.

According to this equation, in a test for functionality it is necessary to know only the functionality of the crosslinking agent, the ratio of the re-

TABLE I
Comparison of Observed and and Calculated Gel Points (Stockmayer's Equation)ᵃ

React. 1 and funct.	React. 2 and funct.	React. 3 and funct.	Equiv. proport.	Av. funct. first reactants	f_E first reactants	Gel point		Calcd. f_E from obsd gel. pt.
						Calcd.	Obsd.	
Tricarballylic acid, 3.0	Adipic acid, 2.0	Diethylene glycol, 2.0	29.3, 70.7, 100	2.22	2.29	0.88	0.91	2.21
Tricarballylic acid, 3.0	Succinic acid, 2.0	Diethylene glycol, 2.0	19.4, 80.6, 100	2.14	2.19	0.92	0.94	2.14
Tricarballylic acid, 3.0	Succinic acid, 2.0	Diethylene glycol, 2.0	40.4, 59.6, 100	2.31	2.40	0.84	0.89	2.27
Epikote 1001, 4.0	Hexahydrophthalic anhydride, 2.0		100, 100	4.00	4.00	0.58	0.58	3.94
Epikote 828, 4.0	Trimellitic anhydride, 3.0		100, 100	4.00	4.00	0.41	0.41	3.97
Octylene oxide, 2.0	Epikote 828, 4.0	Hexahydro-phthalic anhydride, 2.0	15.6, 84.4, 100	3.46	3.69	0.61	0.64	3.47

ᵃ The first three cases were taken from Flory[1a] and the last three from Tanaka and Kakiuchi.[9]

actants, and the extent of reaction of either of the reactants at the gel point. The value obtained is a weighted average functionality. If the spread in functionality is small, f_E will be close to the number-average functionality. In any case, f_E can serve to distinguish between prepolymer lots for specification purposes, provided it can be measured with sufficient precision.

The literature was examined for data that could be used as a test for eq. (5). Table I shows observed gel points taken from the literature in terms of fraction of reactant consumed at the gel point compared with gel points calculated from Stockmayer's equation. The agreement is fairly good. Also shown are values of f_E calculated by this equation from observed gel points. These should be compared with the average functionality of the first reactants or with the f_E value of these reactants calculated from the composition of the mixture. Further work appeared to be justified.

MATERIALS

The prepolymers used in most of the work were CTPB of molecular weights in the range 3000–6000. The samples were obtained from Phillip's Petroleum Company (Butarez CTL-I and II), the General Tire and Rubber Company (Telagen CT), the Thiokol Chemical Company (HC-434), and the B. F. Goodrich Chemical Company (Hycar CTB). Hydroxyl-terminated polybutadiene of molecular weight 2300 was obtained from the Sinclair Refining Company. Liquid polybutadiene was obtained from the Thiokol Chemical Company and from Phillip's Petroleum Company. The crosslinking agents were anhydrous c.p. glycerol, anhydrous 1,4-butanediol from General Aniline and Film Corporation, Eastman-grade sebacic acid and tricarballylic acid from Distillation Products Industries, Epotuf 427-60E (an epichlorhydrin adduct of trimethylol propane of functionality 2.73) from Reichhold Chemicals Incorporated, and Epon X-801 from the Shell Development Company. The last material, an epoxide of functionality 2.86, has been recently withdrawn from the market.

EXPERIMENTAL

Description of Method

An accurately weighed mixture of prepolymer, crosslinking agent, and catalyst was placed in a test tube 25 × 100 mm. A no. 6 spindle for a Brookfield viscometer Model RVF was inserted in the mixture and the top of the test tube was closed with a two-hole stopper. The spindle shaft extended through a center hole in the stopper. Through the side hole of the stopper a glass tube extended approximately 35 mm. from the top. The test tube was placed in an oil bath at a previously adjusted temperature and the spindle connected to the viscometer. Nitrogen was passed slowly through the glass tube during the run. The viscosity of the mixture was

taken at intervals, and drop-size samples were removed during the run and at the gel point. The viscosity approaches infinity very rapidly at this point, and the gel point was considered reached when the viscosity was between 100,000 and 500,000 cp. at the reaction temperature.

When carboxyl-containing prepolymers were employed, the carboxyl content of the resins was usually determined by infrared spectrophotometry with smears on sodium chloride plates. A Perkin-Elmer 21 or 421 instrument was used. Spectra were taken in the region between 1980 and 1450 cm.$^{-1}$. The initial spectrum served as a zero point and was determined at
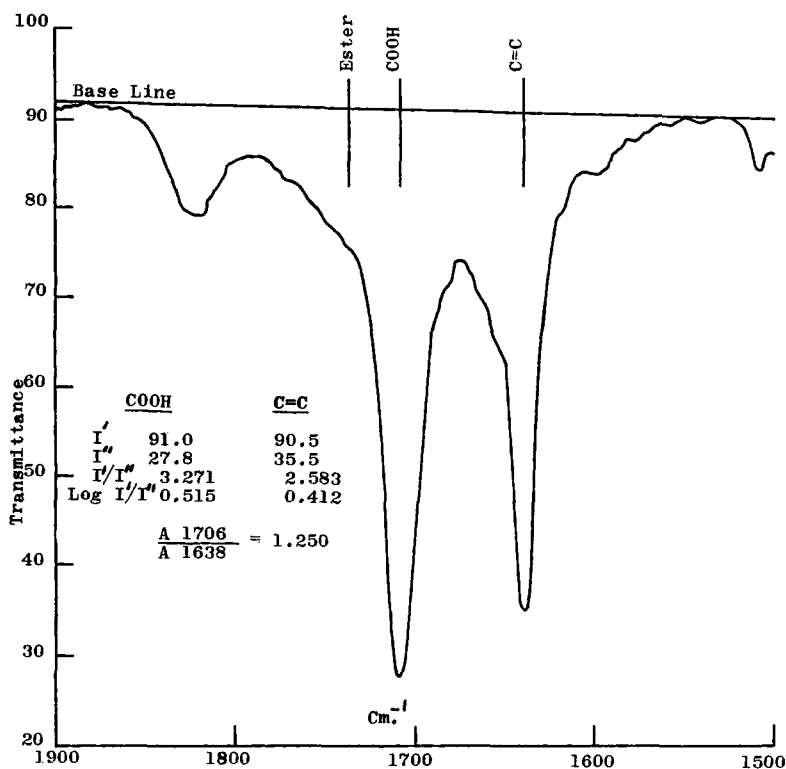

Fig. 1. Partial spectrum of carboxyl-terminated polybutadiene.

least three times from a mixture of prepolymer and catalyst without cross-linking agent. At intervals, depending upon the speed of the reaction, a sample was removed from the complete mixture, and the relative carboxyl content was determined by the baseline method. The absorbance of the carboxyl band at 1708 cm.$^{-1}$ and of the C=C band at 1638 cm.$^{-1}$, which served as a standard, was determined, and the proportion A_{1708}/A_{1638} was computed. A curve was drawn by plotting the numbers obtained against time, and the exact A_{1708}/A_{1638} value was determined at the gel point.

The relative percentage of carboxyl groups that had not reacted, at the gel point, was calculated according to the following:

Unreacted COOH $\%$ = $(A_{1708}/A_{1638}$ at gel point $\times$ 100$)/$
$$(A_{1708}/A_{1638} \text{ at zero time})$$

A typical spectrum and calculation is shown in Figure 1. When epoxides and carboxyl groups react, esters are formed. The ester absorption band is slightly removed from the carboxyl band at 1737 cm.$^{-1}$ instead of 1706 cm.$^{-1}$. Interference from the ester band can reduce the accuracy of the determination beyond the gel point, but it was possible to determine the carboxyl content up to 70% reaction of the initial number of carboxyl groups.

Determination of the carboxyl content at the gel point was carried out principally by infrared methods. Some work was done to see whether titration of carboxyl groups with standard base was sufficiently accurate for functionality measurements. One difficulty with the titration method lies in the time required to withdraw a viscous aliquot from the reaction mixture. The mixture is so viscous when approaching the gel point that a minute or two may be required to remove a sample large enough to titrate. In that time the reaction has proceeded sufficiently to introduce a significant error. Phenolic antioxidants are often present in commercial prepolymers. These react with base and may or may not react with epoxides or aziridine crosslinking agents. To remove this uncertainty the prepolymers must be purified.

Functionality measurements were carried out on several lots of CTPB by both infrared and base titration methods. Samples were titrated with sodium methylate in pyridine solution with thymol blue as indicator. Five determinations gave a functionality number of 2.08 ± 0.05 by titration, which compared with 2.14 by infrared analysis. At best the titration method cannot be considered as accurate as the infrared method.

Calibration of Infrared Method

A simple Beer's-law calculation shows that the olefin absorbances and the extinction coefficients of the carboxyl and olefin groups cancel out in the infrared procedure described above. However, the absorbance for zero carboxyl does not cancel out. The calculated result therefore depends on the position of the baseline, and a calibration was considered necessary.

The extinction coefficient of the olefin band at 1638 cm.$^{-1}$ varies with the structure at the double band, becoming greater as the proportion of vinyl structure increases. Hence calibration was carried out by making single samples react for varying lengths of time and determining the carboxyl content by titration with base. Figure 2 shows the ratio of the COOH absorbance of such a sample to that of the 1638 cm.$^{-1}$ band as a function of the chemically determined COOH content. The baseline employed was that shown in Figure 1. The data extrapolate linearly to zero carboxyl Hence the baseline chosen is correct.
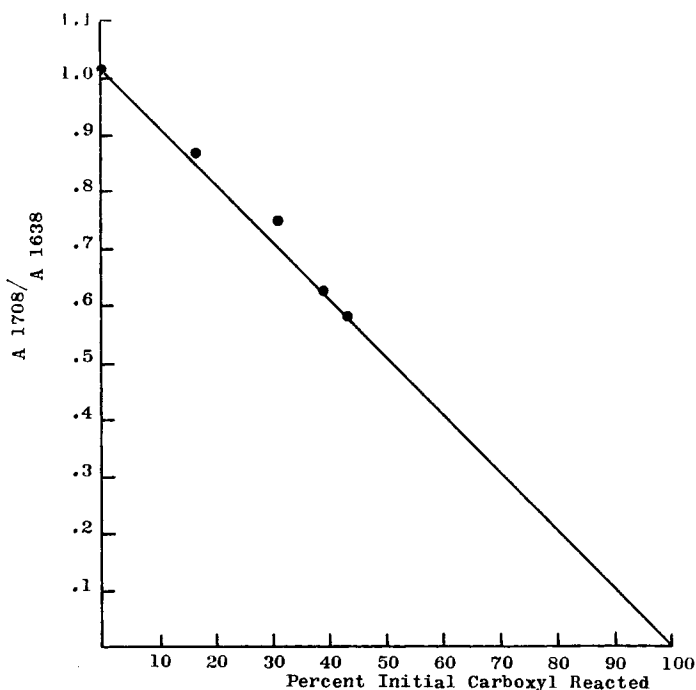
Fig. 2. Relative carboxyl group absorbance as a function of carboxyl content.

Crosslinking Agents

For use in a functionality test a crosslinking agent is needed that undergoes no changes during the reaction and reacts with the prepolymer in only one way. The crosslinking agent should have a functionality not very much less than 3, so that gelation will occur in a reasonable time and will occur when prepolymers with functionalities of less than 2 are being tested. Tris[1-(2-methyl)aziridinyl] phosphine oxide (MAPO) was found to homopolymerize so that its functionality varied from 2.96 to 3.4 at the time of gelation.[11] Such a material is unsuitable.

Experience showed that Shell's Epon X-801 had the necessary stability and freedom from side reactions to make it an ideal candidate for this use. However, it will no longer be commercially available. Molecular weight and equivalent-weight determinations gave a value of 2.86 for its functionality. Much of the work was done by using this material, usually with 1% ferric acetyl acetonate as catalyst at 120°C.

Epotuf 427-60E, produced by Reichhold Chemicals, Inc., was also employed. The molecular weight, determined by a vapor-pressure osmometer, was 448, and the equivalent weight was 164, yielding a number-average functionality of 2.73. Epotuf 427-60E and Epon X-801 were used to determine the functionality of one sample of CTPB. Ferric acetyl acetonate was present as catalyst. The reactions were carried out at

120°C. By means of the number-average epoxide functionalities given above, the prepolymer was found to have a weight average functionality of 2.17 in the Epotuf 427-60E reaction and 2.14 in the Epon X-801 reaction. When chromium naphthenate was used as the catalyst, Epotuf 427-60E acted as a higher-functionality material. From the previously determined 2.17 for the prepolymer the functionality of the Epotuf 427-60E was found to be 3.14 in this case. Although ferric acetyl acetonate promotes atmospheric oxidation, the extent of oxidation in these measurements is slight, and the material is to be preferred to chromium soaps.

Table II gives some results obtained by using Epon X-801 with a functionality of 2.86 and glycerol with a functionality of 3.00 as curing agents. The functionality number of the resin is approximately the same, whether calculated from the epoxide reaction or from the glycerol reaction.

Tricarballylic acid was found satisfactory for the functionality determinations of hydroxyl-containing prepolymers. The reactions were carried out at 150°C. without a catalyst and were followed by titration of the carboxyl groups of the tricarballylic acid. Because of the insolubility of this acid in some resins stirring was employed during the reaction, until the mixture became homogeneous. Titration in this case is preferably carried out in tetrahydrofuran or in pyridine.

TABLE II
Functionality of CTPB

	Epoxide reaction			Glycerol reaction		
Lot no.	Gel time, min.	COOH react., %	f_E	Gel time, f_E	COOH react., %	f_E
CTPB-H	290	61.9	2.40	24	59.8	2.40
CTPB-J	242	62.6	2.37	26.5	60.2	2.38
CTPB-K	152	52.6	2.95	24.5	50.3	2.97
CTPB-L	136	62.4	2.38	19	60.2	2.38
CTPB-M	152	64.6	2.29	20	62.3	2.29
CTPB-N	178	66.0	2.24	18.5	64.2	2.22

TABLE III
Theoretical and Observed Acid Functionalities in the Sebacic Acid–
Tricarballylic Acid–1,4-Butanediol System

Sebacic acid, moles	Tricarballylic acid, moles	Gel time at 150°C., hr.	COOH react., %	f_N	f_E	f_{obs}
0.1	0.025	18.1	87.9	2.20	2.27	2.29
0.1	0.05	8.78	83.3	2.33	2.43	2.44
0.05	0.05	6.33	79.0	2.50	2.60	2.60
0.05	0.1	4.25	76.0	2.67	2.75	2.74
0.025	0.1	3.41	73.5	2.80	2.86	2.86

Comparison of Theoretical and Observed Values

Two series of experiments were carried out with first mixtures of sebacic acid (SA) and tricarballylic acid (TCA) in various ratios, these reacting with 1,4-butanediol at 150°C., and second mixtures of sebacic acid (SA) and stearic acid in various ratios, these reacting with trimethylol propane (TMP) at 150°C. No catalyst was used. This system allowed calculation of functionality in advance and enabled a comparison of theoretical and observed values. Table III and Figure 3 show the results obtained.
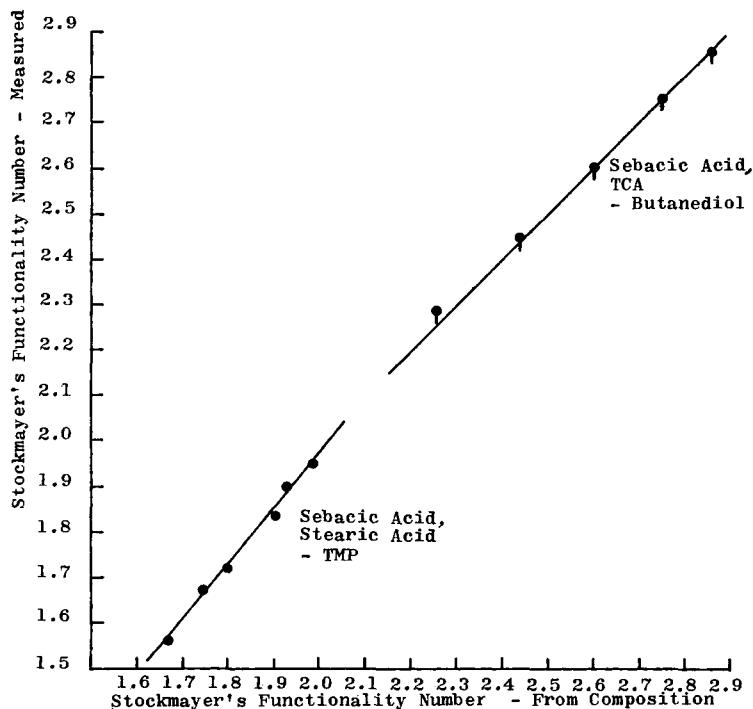

Fig. 3. Comparison of observed and theoretical functionality numbers.

The equations for calculating the number-average functionality f_N and the weighted average functionality f_E are:

$$f_N = (\text{moles SA} \times 2 + \text{moles TCA} \times 3)/\Sigma \text{ moles}$$

$$f_E = (\text{moles SA} \times 2^2 + \text{moles TOA} \times 3^2)/(\text{moles SA} \times 2$$

$$+ \text{moles TCA} \times 3)$$

where SA is sebacic acid and TCA is tricarballylic acid. It can be seen that the observed functionalities f_{obs} fit very well with the theoretical weight-average functionalities, as expected from the theory for the first series with functionality above 2.

When the functionality was below 2, although the measured values were close to the known values, there was a discrepancy that was not observed in the functionality ranges above 2.0, and error appeared to increase with lowering functionality number. Even so, the error was only 0.1 of the functionality value at a functionality of 1.6.

Influence of Dilution

The influence of dilution on the functionality value obtained is crucial to the use of the method. It has long been known that the gel point curing the cooking of alkyds occurs at greater extents of reaction than are predicted by the theories used here. This phenomenon has been investigated by Price et al.[12] and by Bobalek et al.[13] The first-named cite results given by Stockmayer and Weil, who investigated the effect of dilution on the reaction of pentaerythritol with adipic acid. They found that when the extent of reaction at gelation was extrapolated to infinite concentration of reacting groups, the theoretical extent of reaction was obtained.

One would conclude that the gelation theory is essentially correct but that intramolecular bond formation can occur, which is favored by dilution, or that, more accurately, the chances of intermolecular reactions are decreased by dilution. Thus, if intramolecular reactions are occurring, dilution should yield lower measured functionality values.

The influence of the structure of the reactants cannot be neglected. Alkyd resins are commonly made in reactions of rather small molecules, so that in the first stages of reaction the functional groups are still close together. Most of the work on gel point theory has been done with systems of this type. In the work reported here, however, the prepolymers had molecular weights in the range 3000–6000, and in most cases the functional groups were located on the two ends of the chains. As the functionality increases beyond 2, the functional groups are closer together, and the influence of dilution should increase.

The results shown in Tables II and III were obtained with mixtures of undiluted prepolymers. CTPB of molecular weight 5000 was diluted in various ratios with nonfunctional polybutadiene. Figure 4 shows the influence of dilution on the gel times when the ratio of CTPB to nonfunctional polybutadiene is varied.

TABLE IV
Independence of the Functionality Determination on Dilution

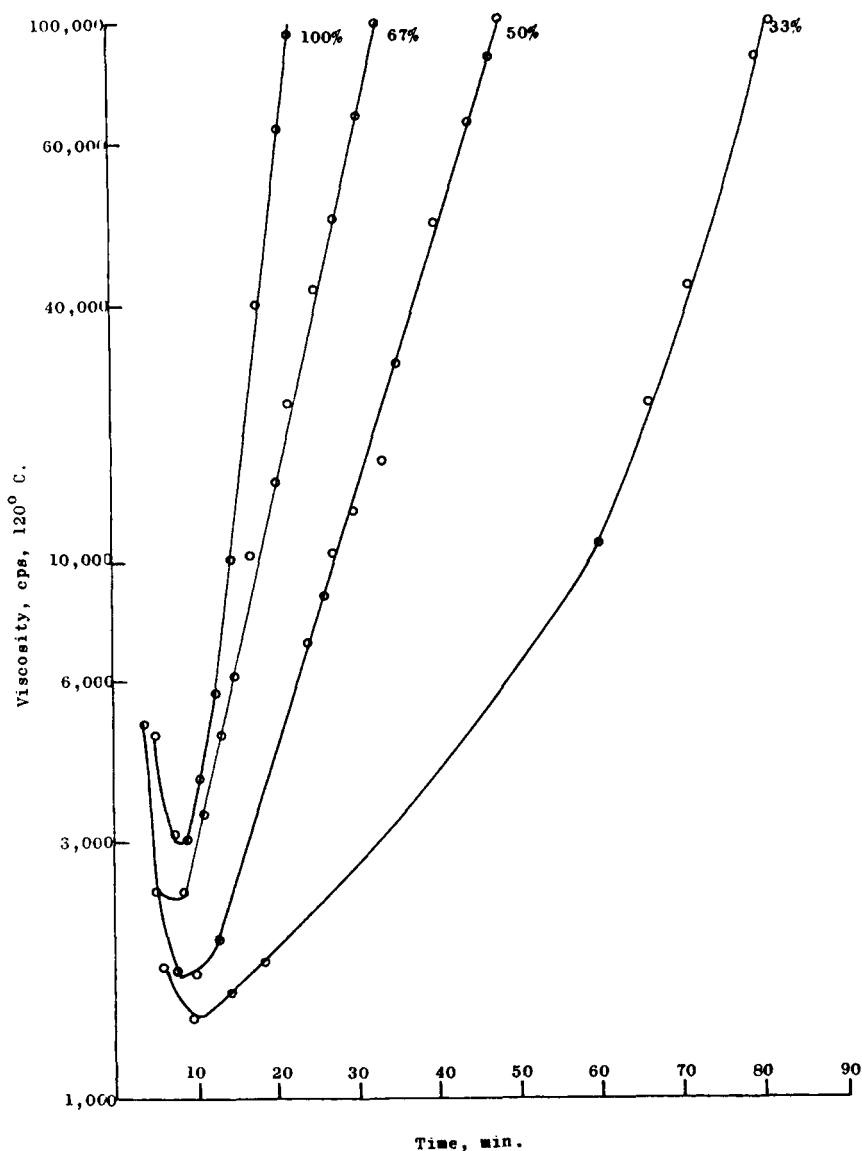| CTPB, g.	Poly-butadiene, g.	CTPB: poly-butadiene	Gel time, min.	COOH react., %	f_E
25	—	1:0	24	65.4	2.26
16.7	8.3	1:0.5	35	65.2	2.26
12.5	12.5	1:1	51	64.6	2.28
8.3	16.7	1:2	84	65.5	2.26

Fig. 4. Variation of gel time with concentration of CPTB in polybutadiene.

The more diluted the CTPB, the longer the gel time, but in all cases there is the same rapid increase of the viscosity during the approach to the gel point.

Figure 5 shows the decrease of the carboxyl groups during the reaction in different mixtures. The reaction was followed by infrared analysis. The ratio of CTPB to nonfunctional polybutadiene is written beside the corresponding curves. A characteristic of all the curves is a leveling off on the
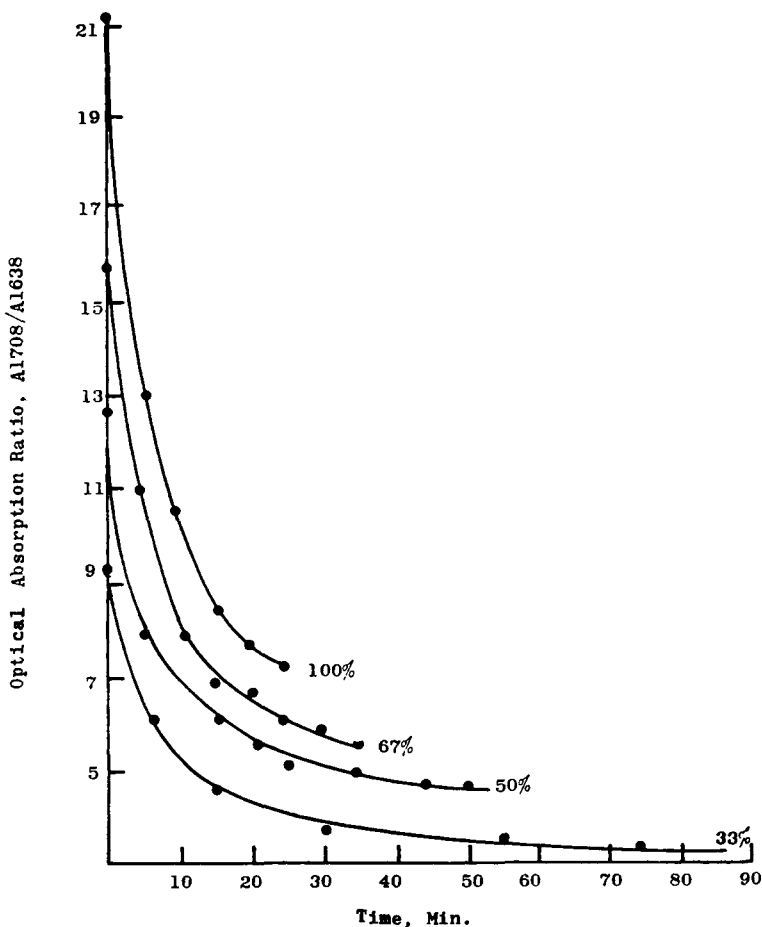
Fig. 5. Decrease in carboxyl content with time at various concentrations of CTPB.

approach to the gel point. The results and the calculated functionalities
are given in Table IV.

The functionality is constant over a wide range and the method of deter-
mination is therefore independent of dilution at least at this prepolymer
molecular weight and functionality.

Variation in Reactant Ratio

It is frequently desirable to mix reactants in other than a stoichiometric
ratio. The effect of varying the reactant ratio was investigated. For the
reaction between CTPB-Lot G and Epon X-801, in which r, the ratio be-
tween epoxide and carboxyl groups, was changed continuously, the amount
of carboxyl groups reacting up to the gel point was determined by infrared
analysis. The results are listed in Table V. The functionality of the
polymer was calculated according to eq. (5) by using a functionality of 2.86

TABLE V
Calculated Functionality as a Function of Reactant Ratio

CTPB, g.	Epon X-801, g.	r	Gel time, min.	P_{COOH}, %	f_E
25	0.405	0.6	248	46.5	2.49
25	0.540	0.8	220	54.1	2.47
25	0.675	1.0	168	60.1	2.49
25	0.810	1.2	152	66.1	2.48
25	0.945	1.4	178	70.2	2.52

for the epoxide. The polymer functionality was fairly constant over a wide range.

Effect of Varying Initial Viscosity

A prepolymer reacting with a chain-extending agent may, until gelation occurs, be regarded as a solution of a high polymer in a prepolymer solvent. Data of Streeter and Boyer[14] show that the viscosity of polymer solutions of constant concentration varies linearly with the viscosity of the solvent employed. Hence it is of interest to see how the viscosity and gel time of prepolymers during cure varies with the initial viscosity of the prepolymers and with their functionalities.

Table VI shows first a set of three CTPB prepolymers of increasing initial viscosity but of the same functionality. Viscosity increased faster during cure when the initial viscosity was high. The gel time is, therefore, dependent on initial viscosity. However, the extent of reaction at the gel point was not dependent on initial viscosity.

The second set is of three prepolymers of nearly the same initial viscosity but with different functionality numbers. Viscosity increased faster during cure, gel times decreased as the functionality increased, and the extent of reaction at the gel point decreased even though the viscosity was nearly constant initially.

TABLE VI
Comparison of Functionality and Initial Viscosity with Gel Time

CTPB sample	COOH equiv. wt.	Visc. at 25°C., P.	f_E	Gel time, min.
At constant f_E and varying initial viscosity, epoxide reaction at 120°C.:				
CTPB-A	4090	220	2.15	331
CTPB-B	4050	278	2.14	284
CTPB-C	4260	324	2.18	214
At constant initial viscosity and varying f_E, aziridine reaction at 105°C.:				
CTPB-D	4330	232	2.27	161
CTPB-E	4070	225	2.35	149
CTPB-F	4290	230	2.62	139

One must conclude that the gel time and the rate of the viscosity increase vary both with functionality and initial viscosity, while the rate of reaction and the extent of reaction at the gel point are dependent on the functionality but not on the initial viscosity.

Hydroxyl-Containing Prepolymers

The determination of the functionality of a hydroxyl-terminated polybutadiene, Sinclair R45, was carried out with two curing agents, tricarballylic acid and tolylene diisocyanate. Table VII gives the results and conditions.

TABLE VII
Functionality Determination of Hydroxyl-Terminated Polybutadiene

Curing agent	Gel time, hr.	Curing agent react., %	f_E
Tricarballylic acid	6.1 at 150°C.	55.9	2.60
Tolylene diisocyanate	4.86 at 60°C.	79.7	2.58

Because of the insolubility of tricarballylic acid in Sinclair R45 stirring was employed until the whole mixture was homogeneous.

The $N=C=O$ content was determined by infrared analysis with the use of the isocyanate band at 2259 cm.$^{-1}$ and the C—H band at 2840 cm.$^{-1}$ as standards. The zero point could not be determined in the original mixture because of the very rapid reaction of the $N=C=O$ groups at room temperature. A separate mixture of nonfunctional polybutadiene and tolylene diisocyanate therefore was made (same composition as the reaction mixture), and the zero point was determined. No amide I band at 1730 cm.$^{-1}$ appeared in this mixture within the first-15 min.

Although gelation definitely occurs in the Sinclair R45–tolylene diisocyanate system, the determination of the gel point is not as precise as in the other reactions with acids or epoxides as curing agents. In these reactions the viscosity increases very rapidly on the approach to the gel point, whereas in the isocyanate reaction viscosity increases more slowly. The reaction was stopped and gelation assumed when the viscosity reached 2,000,000 cpoise. This assumption can be made without introducing too high an error, because of the leveling off of the reaction rate. The slow rate of viscosity increase probably results from the low average functionality of the system, about 2.3.

Tricarballylic acid with functionality 3.0 is to be preferred as a crosslinking agent. The extent of reaction was followed by titration of the carboxyl groups in pyridine. The rate of viscosity increase at the gel point was more rapid than when tolylene diisocyanate was used.

Weight-Average Molecular Weight

Stockmayer's theory results in a weighted average functionality from which a weight-average molecular weight can be obtained. This weight

average is not that ordinarily regarded as, the weight-average molecular weight. Expressing $f_E \times E$, where E is the equivalent weight, and the weight-average molecular weight M_w in terms of moles n, E, and functionality f, one obtains the following:

$$M_w = \Sigma n_i E_i^2 f_i^2 / \Sigma n_i E_i f_i = \Sigma n_i E_i^2 f_i^2 / \Sigma n_i E f_i$$

$$f_E \times E = \Sigma n_i E^2 f_i^2 / \Sigma n_i E f_i$$

where $E = \Sigma n_i E_i / f_i / \Sigma n_i f_i$, and the subscript i expresses a value for a particular species. Therefore $f_E \times E$ is an average molecular weight which, like the viscosity average, lies between the weight-average and the number-average. It is less than the viscosity average and close to the root-mean-square molecular weight. One can obtain $f_E E$ by multiplying the equivalent weight, determined by titration, by the calculated functionalities. Table VIII shows the molecular weights thus obtained compared with the molecular weights obtained by intrinsic-viscosity measurements and calculated according to[15] $[\eta] = 0.00080 M^{0.61}$ in cyclohexane at 30°C. An agreement within $\pm 10\%$ was observed. It is suggested that this method may be of some general interest as an alternative means of obtaining weighted average molecular weights.

TABLE VIII
Molecular Weights of CTPB

Sample no.	Equiv. wt.	f_E	M_w	$[\eta]$	M_w visc.
CTPB-H	2390	2.40	5740	0.144	5000
CTPB-J	2960	2.38	7100	0.191	7800
CTPB-K	3970	2.96	11750	0.230	10700

Other applications of the use of functionality numbers from gel point measurements have been in following the kinetics of the reaction[11] between CTPB and tris[1-(2-methyl)aziridinyl] phosphine oxide and in determining chain extension before the gel point in systems containing both difunctional and higher-functionality curatives.

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