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David M. French[a]
[a] White Oak Laboratory, Propellants Division Propellants Chemistry Branch Naval Surface Weapons Center, Silver Spring, Maryland

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Crosslink Density from Sol-Gel Contents

DAVID M. FRENCH

Propellants Division
Propellants Chemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

ABSTRACT

Experimental results showed that the crosslink density of polymeric stocks may be calculated from values of the gel content based on the reactive portion of the stocks, that is, exclusive of plasticizers and fillers. Where entanglements may be neglected, the crosslink density is directly proportional to functions of the gel and sol contents. Four such functions were found. Three of these were theoretically derived relations in the literature and these were modified to provide equations connecting crosslink density and the weight fraction of gel W_g and connecting extent of reaction and W_g for condensation polymers. Although followed up to moderate degrees of cure, the Flory relation was shown not to be in proper form. A fourth but simpler relation, based on an empirical correlation, was found between crosslink density and gel content, namely, that the crosslink density was directly proportional to the square of the gel fraction divided by the first power of the sol fraction. The constant of proportionality was 0.0065 meq/g for three-functional networks. When placed in terms of extent of reaction, this equation was found to yield nearly the same gel content relative to extent of reaction as that of Charlesby and there was a smaller coefficient of variation of experimentally determined proportionality constants.

INTRODUCTION

Various workers [1-13] have investigated the theory of the development of the gel fraction during condensation polymerization as a function of crosslink density and extent of reaction. Although rubber chemists for years have used sol-gel determinations as qualitative measures of the state of cure, the use of sol-gel values to determine absolute crosslink densities in a quantitative manner does not seem to have been attempted. Most crosslinked polymers in practical use contain fillers which influence stress-strain properties. Sol-gel measurements have the great advantage that nonreinforcing fillers do not change the proportion of gel to sol, although correction must be made for the presence of plasticizers. The present work was undertaken to see how sol-gel values were related to crosslink density.

MATERIALS AND TEST METHODS

Elastomeric gum stocks were prepared from various carboxyl-terminated polybutadienes (CTPB), hydroxyl-terminated polybutadienes (HTPB), and poly(propylene glycol) with the propylene oxide adduct of glycerol. Mapo, Epon 812, and Epotuf STF-6 were used as coreactants or crosslinking agents for the CTPB stocks, Isonate 143L for the HTPB stocks, and trimethyl hexamethylene diioscyanate for the propylene oxide prepolymers. In some cases, the plasticizers Flexol 3GH, Conoco oil H25, liquid polybutadiene, and dioctyl sebacate were used. These materials are identified in Table 1. All reactants were in stoichiometric proportion. The stocks were fully cured. Some properties are given in Tables 2 and 3.

In addition, two series of stocks were prepared in which the cure time was varied. These employed Butarez CTL-II, a carboxyl-terminated polybutadiene, and Hycar CTBN, a carboxyl-terminated butadiene-acrylonitrile copolymer (10%). The composition and cure time are given in Table 4.

Some properties of series A and B stocks are shown in Table 5.

TABLE 1. Materials Used

Trade name	Chemical name	Source	Active group content (meq/g)
Butarez CTL-I	Carboxyl-terminated polybutadiene	Phillips	0.245
Butarez CTL-II	Carboxyl-terminated polybutadiene	Phillips	0.381, 0.364
HC-434	Carboxyl-terminated polybutadiene	Thiokol	0.512
Hycar CTBN	CTPB-acrylonitrile (10%)	Goodrich	0.50
Telagen CT	Carboxyl-terminated polybutadiene	Gen. Tire	0.370
Telagen HT	Hydroxyl-terminated polybutadiene	Gen. Tire	0.98
Telagen HT-S	Hydroxyl-terminated polybutadiene, saturated	Gen. Tire	0.92
Butarez HTS	Hydroxyl-terminated polybutadiene	Phillips	0.37
P 2010	Poly(propylene oxide)	BASF-Wyandotte	1.00
GP 1530	Poly(propylene oxide) adduct of glycerol	BASF-Wyandotte	1.89
Mapo	Tris[1-(2-methyl)-aziridinyl] phosphine oxide	Nav. Ord. Sta.	13.6
Epotuf STF-6	Glycidyl ether of trimethylol propane	Reichhold	6.9
Epon 812	Glycidyl ether of glycerol	Shell	5.99
Isonate 143L	Modified 4,4'-diphenyl methane diisocyanate	Upjohn	7.1
TMDI	Trimethyl hexamethylene diisocyanate	Thorson	9.43
Flexol 3GH	Triethylene glycol di(2-ethyl) butyrate	Union Carbide	
Conoco H-25	Hydrocarbon oil	Continental Oil	
FeAA	Ferric acetyl acetonate		

TABLE 2. Sol-Gel Data on Completely Cured Stocks

		Gel fraction[a]	Sol fraction[a]	W_g/W_s	q(BF) (meq/g)
CTPB					
Telagen CT		0.888	0.112	7.93	0.064
HC-434		0.935	0.065	14.4	0.121
HC-434		0.733	0.267	2.7	0.018
Butarez CTL-I		0.86	0.14	6.1	0.051
Butarez CTL-I		0.81	0.19	4.3	0.043
Butarez CTL-II		0.922	0.078	11.8	0.121
HTPB					
Telagen HT-S		0.367	0.633	0.58	0.018
Telagen HT		0.074	0.926	0.08	0.010
Butarez HTS		0.038	0.962	0.04	0.011
Polyether-Polyurethane					
PPG-GP1530	A	0.940	0.060	15.7	0.111
PPG-GP1530	B	0.899	0.101	8.9	0.087
PPG-GP1530	C	0.907	0.093	9.6	0.063
PPG-GP1530	D	0.807	0.193	4.2	0.040
PPG-GP1530	E	0.664	0.336	2.0	0.014

[a] Based on reactives.

Where the stocks were not too soft, crosslink densities were determined by the solvent-swollen compression modulus technique of Cluff, Gladding, and Pariser [14]. The crosslink density of the unextracted stock is given by Eq. (1):

$$X_d = 2h_0SW_g/3\pi r^2 RT\rho FV_r{}^{1/3} \qquad (1)$$

where X_d is crosslink density (moles or equivalents/g), h_0 is height of unswollen sample (cm), S is the slope of a plot of sample height versus applied weight (g/cm), W_g is the weight fraction of gel, r is

TABLE 3. Crosslink Density and Gel-Sol Ratio in Fully Cured Stocks

X_g (meq/g)	Plast. fraction P	$\frac{X_g}{(1 - P)}$	Gel fraction W_g	$\frac{W_g}{(1 - P)}$	Sol fraction	$\frac{\text{Gel}}{\text{Sol}}$	$\frac{\text{Gel}^2}{\text{Sol}}$	X_d (meq/g)
0.0111	0.286	0.0155	0.535	0.750	0.250	3.00	2.25	0.0116
0.0179	0.286	0.0251	0.537	0.752	0.248	3.03	2.28	0.0189
0.0174	0.286	0.0244	0.560	0.784	0.216	3.63	2.85	0.0191
0.0153	0.286	0.0215	0.561	0.786	0.214	3.67	2.88	0.0169
0.0245	0.450	0.0446	0.483	0.878	0.122	7.20	6.32	0.0391
0.0280	0.450	0.0509	0.479	0.871	0.129	6.75	5.88	0.0443
0.0155	0.450	0.0281	0.462	0.840	0.160	5.25	4.41	0.0236

TABLE 4. Composition and Cure of Stocks Used

	Active group content (meq/g)	Series A	Series B
Butarez CTL-II, 2BJ3	0.364	100.0	–
Hycar CTBN, 34-35-09	0.50	–	100.0
Epon 812, 6RHG6,	5.99	6.08	8.35
Ferric acetyl acetonate	–	0.05	0.05
		106.13	108.40
Cure temperature (°C)		130	120
Time of cure, (hr)		6.5	3.5
		7.5	4.5
		9	5
		11	6
		12.5	6.5
		16	7.5
		23	14
		61	23
			77

the radius of the unswollen sample (cm), R is the gas constant (84780 g-cm), ρ is polymer density (g/ml), F is network functionality, T is temperature (°K), and V_r is the volume fraction of gel rubber in the unswollen sample.

If there is no plasticizer, $W_g/V_r^{1/3}$ becomes $W_g^{2/3}$. When the crosslink density is desired in the unplasticized state, X_d is divided by 1 minus the fraction of plasticizer, and W_g is based on the reactive portion of the stock. Cylinders of the stocks were covered with toluene for a week. The solvent was replaced with fresh solvent once or twice during the week to remove the sol fraction.

Gel content was first measured by continuous extraction with methylene chloride in a Soxhlet apparatus using fairly large samples. This

TABLE 5. Crosslink Density Functions of Series A and Series B Stocks

Stock	Cure time (hr)	Crosslink density (gel + sol) (meq/g)	Gel content (%)	$\frac{\text{Gel}}{\text{Sol}}$	W_g^2/W_s[a]	V_2[b]	$V_2^{5/3}$
A	6.5		0.32	0.003	0	0.0024	0.0019
	7.5		4.0	0.042	0	0.0082	0.00034
	9		15.9	0.19	0.03	0.013	0.00072
	11		49.0	0.96	0.47	0.0299	0.00286
	12.5	0.00506	57.8	1.37	0.79	0.0423	0.00513
	16	0.0192	77.6	3.35	2.60	0.0862	0.0168
	23	0.0347	85.5	5.90	5.0	0.116	0.0276
	61	0.0393	89	8.1	7.2	0.150	0.0423
B	3.5		0	0	0	0	0
	4.5		0.23	0.002	0	0.015	0.00091
	5		38.3	0.62	0.24	0.0151	0.00093
	6	0.0025	41.2	0.70	0.29	0.0321	0.00325
	6.5	0.00498	58.8	1.42	0.84	0.0561	0.00822
	7.5	0.00615	61.7	1.61	0.99	0.0625	0.00985
	14	0.00164	74.3	2.89	2.15	0.0985	0.0210
	23	0.0286	83.7	5.13	4.29	0.134	0.0350
	77		86.2	6.25	5.39	0.144	0.0394

[a] W_g is the weight fraction of gel; W_s is the weight fraction of sol.

[b] V_2 is the volume fraction of polymer in the xylene-swollen gel.

method proved imprecise and gave high results. The method finally adopted was to use samples weighing from 200 mg for high gel samples up to 1.0 g for stocks of low gel content. The accurately weighed samples were cut into pieces weighing not over 30 mg each and placed in 50 ml of mixed xylene for a period of a week. The xylene was changed on the second and fifth day. The solvent-swollen samples were weighed, and the solvent was removed by vacuum drying at 70° C. From the initial, solvent-swollen, and final dry weights were calculated the gel content and the volume fraction of polymer (V_2) in the solvent-swollen gel.

DISCUSSION

Development of Previous Work

Flory [1] derived relations between the content of sol fraction and the probability that a polymer chain ends in a branch unit. For the particular case where difunctional and trifunctional compounds react in stoichiometric proportion with difunctional compounds, his relation may be put in the form

$$e_g = 1/[1 + (f_w - 2) W_s^{1/3}]^{1/2} \tag{2}$$

where e_g is the extent of reaction in the gel, W_s is the weight fraction of sol, and f_w is the weight-average functionality of the prepolymers. The mathematics involved in the transformation are detailed elsewhere [1, 15].

Miller and Macosko [13] and Gordon [8] used different approaches but arrived at the same result as Flory. The former extended the results to a relation between sol content and crosslink density. For three functional networks this becomes:

$$X_d = X_g W_g = CW_g [1 - W_s^{1/3}]^3 \tag{3}$$

where X_d is the average crosslink density of gel and sol, taking the crosslink density in the sol as zero, X_g is the crosslink density in the gel, W_g is weight fraction of gel, and C is a constant. For four-functional networks, the equation is a quartic.

As will be shown, the Eq. (3) is followed up to moderate degrees of cure. Although not obvious, the form of Eq. (2) is incorrect. Equation (2) gives the relation between the extent of reaction in the gel and the sol content. Flory's theory also allows the calculation

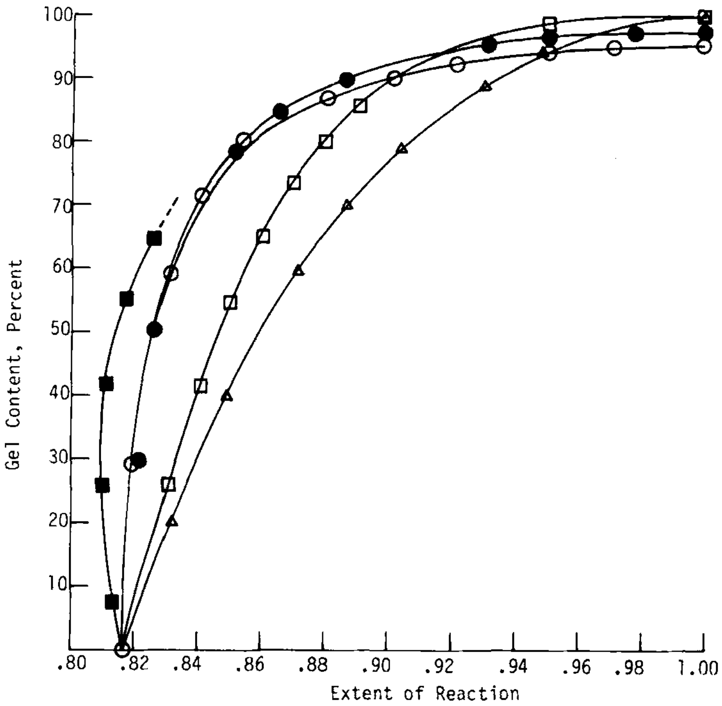

FIG. 1. Calculated development of the gel, comparison of various relations: (○) gel, present study; (●) gel, Charlesby [3-5]; (□) gel, Flory [1]; (■) gel + sol, Flory [1]; (△) gel, Scanlon [6, 7].

of the extent of reaction in the sol e_s from the sol content. It is then possible to calculate the average extent of reaction by using the relation

$$e = e_g W_g + e_s W_s \tag{4}$$

where e is the average extent of reaction, gel and sol.

Figure 1 shows a hypothetical case of a compound of weight-average functionality of 2.5 reacting with a compound of functionality of 2.0. The gel content is given as a function of extent of reaction. It is seen that the average extent of reaction including gel and sol initially decreases after the gel point–an impossibility.

Charlesby [3, 4] Charlesby and Pinner [5], and subsequently Gordon [8] deduced that the number of crosslinked segments per number-average initial molecule was proportional to $1/(W_s + W_s^{1/2})$ in a tetrafunctional network. Thus the number of crosslinks per gram of gel would be proportional to $2/F(W_s + W_s^{1/2})$, where F is the network functionality. However, if there is no gel and $W_s = 1$ this expression does not reduce to zero. If the reciproal of $(W_s + W_s^{1/2})$ is plotted against the crosslink density in the gel, at $X_g = 0$, $1/(W_s + W_s^{1/2}) = 0.5$. The correct equation of the relation between X_g and $W_s + W_s^{1/2}$ is therefore:

$$[2/(W_s + W_s^{1/2})] - 1 = (1/k)\,X_g$$

or

$$[2 - (W_s + W_s^{1/2})]/(W_s + W_s^{1/2}) = (1/k)\,X_g \tag{5}$$

Therefore

$$X_d = X_g W_g$$

$$= kW_g[2 - (W_s + W_s^{1/2})]/(W_s + W_s^{1/2}) \tag{6}$$

Here the proportionality constant k includes an inverse network functionality term. This relation reduces X_g to zero if W_g is zero and predicts that W_s cannot reach zero.

If the crosslink density is known as a function of the extent of reaction producing the network, Eq. (6) may be transformed to a relation between extent of reaction and sol or gel content.

French deduced [16] for the crosslinking of telechelic prepolymers that

$$X_g = 2q(BF)[(e_g - e_c)/(1 - e_c)] \tag{7}$$

where e_c is the extent of reaction at the gel point, q is the prepolymer reactive group concentration, and (BF) is a branching function which for two- and three-functional materials reacting in stoichiometric proportions with two- and three-functional materials takes the form $1 - (1/f_1) - (1/f_2)$; f_1 and f_2 are number-average functionalities of the two species.

Combining Eqs. (6) and (7) yields

$$e_g = e_c + \frac{k[2 - (W_s + W_s^{1/2})]}{W_s + W_s^{1/2}} \left[\frac{1 - e_c}{2q(BF)}\right] \tag{8}$$

Figure 1 shows the course of the same hypothetical reaction used above when plotted according to Eq. (8) on using a value of 0.0124 for k. At 100% reaction, the gel content is slightly below 100%, as it should be. The branching function (BF) was calculated by using a number-average functionality of 2.4, corresponding to a weight-average functionality of 2.5 for a prepolymer mixture containing equal numbers of two- and three-functional reactive groups.

Scanlan [6, 7] derived an equation for the sol content which is similar to that of Flory [1], except that he found

$$W_s = [(1/\alpha) - 1]^2$$

for trifunctional networks rather than $W_s = [(1/\alpha) - 1]^3$ as given by Flory.* Here α is the probability that a polymer chain ends in a branch point. Scanlan's relation may be put in a form similar to Eq. (2) for the extent of reaction in the gel:

$$e_g = 1/[1 + (f_w - 2)W_s^{1/2}]^{1/2} \tag{9}$$

The equation holds only for the particular case where difunctional and trifunctional compounds react in stoichiometric proportion with difunctional compounds. It leads to a slow development of the gel as shown in Fig. 1. Following the reasoning of Scanlan [6, 7] and Miller and Macosko [13], the corresponding relation for the crosslink density will be:

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*Equation (4) of the paper by Scanlan [6] is incorrect and should read, $s = 1$ or $(1 - \alpha)^2/\alpha^2$.

$$X_d = X_g W_g = bW_g[1 - W_s^{1/2}]^3 \tag{10}$$

where b is a constant.

Present Work

As described above, crosslinked stocks were prepared from carboxyl-terminated polybutadiene (CTPB), and hydroxyl-terminated polybutadiene (HTPB) and from polypropylene glycol (PPG) admixed with the propylene oxide adduct of glycerol. Co-reactants in stoichiometric proportion were Epotuf STF-6, Mapo, Epon 812, Isonate 143L, and trimethylhexamethylene diisocyanate as described in Table 1. Gel contents of the fully cured stocks were determined with results shown in Table 2. Functionalities of the CTPB ingredients were known to be mixed, that is, not exactly two or three. The functionalities of these materials were measured by a gel point method [17]. Those of the other prepolymers were taken as 2.0 or 3.0, according to their structure. The expression q(BF) was calculated (see Table 2), where q is the prepolymer reactive group content (meq/g) and BF is the branching function which has the form 1 - $(1/f_1)$ - $(1/f_2)$ for three-functional networks and 0.75 - $(1/2f_1)$ - $(1/f_2)$ for tetrafunctional networks, where f_1 is the prepolymer functionality and f_2 is the coreactant functionality. The expression q(BF) is a measure of the crosslink density in the gel fraction in fully cured stocks [16].

Empirically it was found that q(BF) was a linear function of the ratio of the gel to the sol fraction of the stocks. Figure 2 shows the correlation

$$q(BF) = 0.0086\ W_g/W_s \tag{11}$$

Although the stocks shown in Fig. 2 were fully cured, they differed in ingredient functionality and hence in the final maximum extent of reaction of the functional groups. Because the stocks were fully cured, the extent of reaction did not enter into consideration and is not expressed in Eq. (11). It is certain, however, that any stock before it is fully cured will contain more sol than when fully cured, and the extent of reaction should enter the equation and enter it in such a way as to decrease W_s as the extent of reaction increases. At the maximum extent of reaction, the function containing the extent of reaction should become constant at varying prepolymer and curative

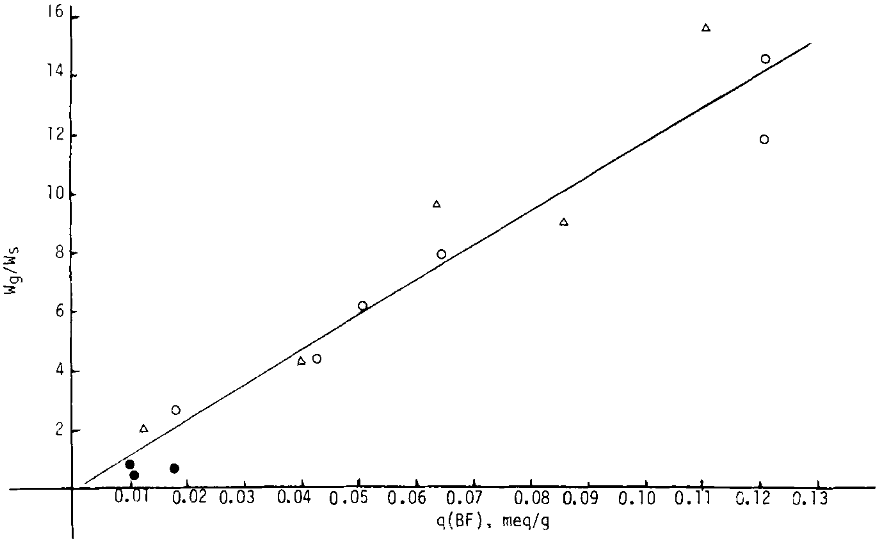

FIG. 2. Variation of gel/sol ratio with prepolymer parameters: (○) polybutadiene, COOH-terminated; (●) polybutadiene, OH-terminated; (△) polyether polyurethane; (—) $q(BF) = 0.0086W_g/W_s$.

functionality since extent of reaction was not found a factor influencing the sol content of fully cured stocks.

As shown in our previous publication [16], the crosslink density of telechelic stocks can be expressed by:

$$X_d = 2q(BF)\,(CDF)W_g$$

where W_g is the weight fraction of gel ($= 1 - W_s$); CDF is a crosslink decrease factor in the gel [$= (e_q - e_c)/(1 - e_c)$], e_g is the extent of reaction in the gel, and e_c is the extent of reaction at the gel point. The crosslink decrease factor increases with extent of reaction but is approximately constant for different stocks at the maximum possible extent of reaction. It is seen that use of the CDF term in Eq. (11) will place it in the proper form to express variation with extent of reaction. The relation will then be:

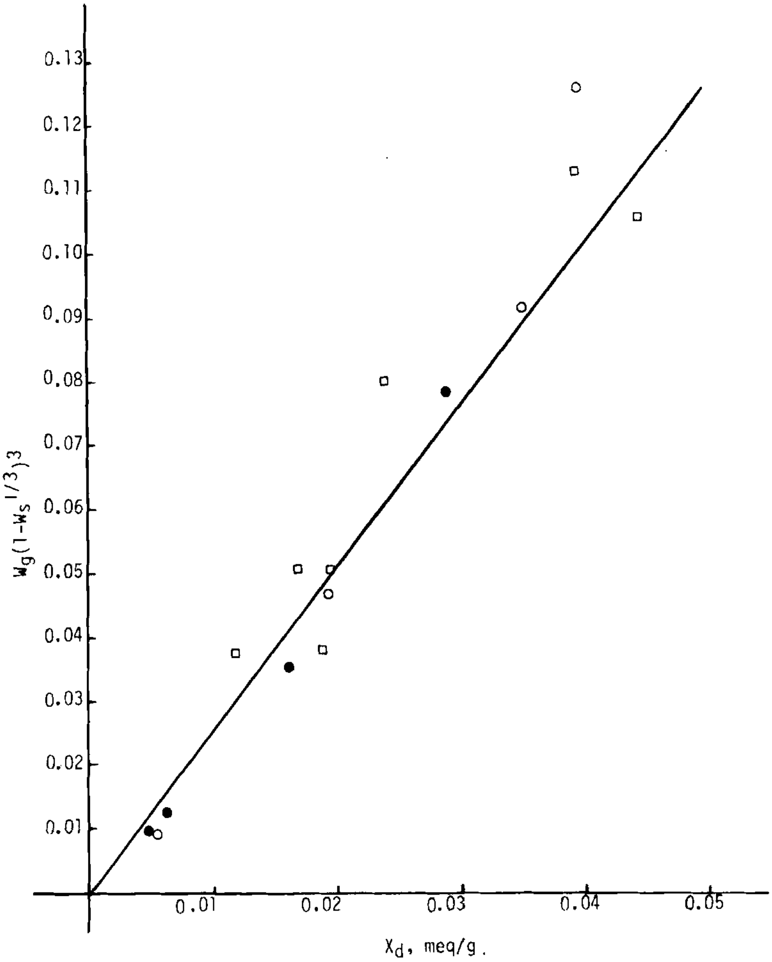

FIG. 3. Crosslink density vs. Flory-Miller, Macosko relation: (○) variation in cure, Butarez CTL-II; (●) variation in cure, Hycar CTBN; (□) fully cured, Butarez CTL-I and CTL-II; (—) $X_d = 0.40W_g(1 - W_s^{1/3})^3$.

$$2q(BF)\,(CDF) = X_g = KW_g/W_s \qquad (12)$$

or

$$X_d = X_g W_g = KW_g^{\,2}/W_s \qquad (13)$$

where K = 2 (0.0086)(CDF) meq/g for three-branched networks.

The branching function (BF) on the left-hand side of Eq. (12) can be shown to vary as the reciprocal of the network functionality. Solving Eq. (12) for W_s in terms of the extent of reaction in the gel, we obtain

$$W_s = 1/[1 + m(e_g - e_c)] \qquad (14)$$

where

$$m = 2q(BF)/K(1 - e_c)$$

The weight fraction of gel was calculated as a function of e_g, a value of K of 0.0065 (as obtained below) being used for the hypothetical case of a mixture of two- and three-functional prepolymer of number-average functionality 2.4 and weight-average functionality 2.5 reacting with a 2.0-functional compound; q was taken as 0.75 meq/g. The curve is shown in Fig. 1 compared with similar curves calculated by using the Flory-Miller, Macosko, Scanlan, and the Charlesby relations. Essentially, Eq. (14) yields the same curve as the modified Charlesby relation, Eq. (8), but is much simpler in form than Eq. (8).

In order to evaluate Eqs. (3), (6), (10), and (13), crosslink densities were determined by the solvent-swollen compression modulus method [14] on Series A and B stocks cured for various times and on the fully cured stocks as described above. Results are given in Tables 3 and 5 and plotted in Figs. 3-6. The constants of proportionality in Eqs. (3), (6), (10), and (13) are 0.40, 0.012, 0.167, and 0.0065 meq/g, respectively, for three functional networks. The constants in Eqs. (6) and (13) involve the network functionality in inverse proportion, while Eqs. (3) and (10) take different forms for tetrafunctional networks, being [13] respectively:

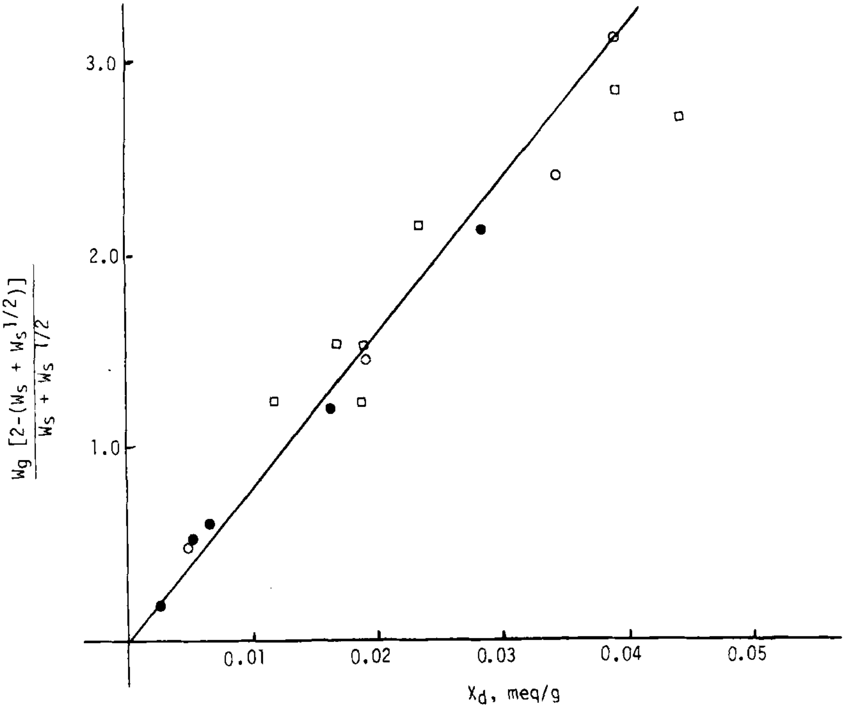

FIG. 4. Crosslink density versus Charlesby function: (○) variation in cure, Butarez CTL-II; (●) variation in cure, Hycar CTBN; (□) fully cured, Butarez CTL-I and CTL-II; (—) $X_d = 0.0124 W_g [2 - (W_s + W_s^{1/2})]/(W_s + W_s^{1/2})$.

$$X_d = c' W_g [0.5 - (0.25 + W_s^{1/3})^{1/2}]^4 \qquad (15)$$

and

$$X_d = b' W_g [0.5 - (0.25 + W_s^{1/2})^{1/2}]^4 \qquad (16)$$

where c' and b' are new constants.

It is not certainly known how the constants vary with polymeric structure. Equation (13) holds for CTPB and HTPB polymers, for butadiene-acrylonitrile copolymers, and for polyether-polyurethanes.

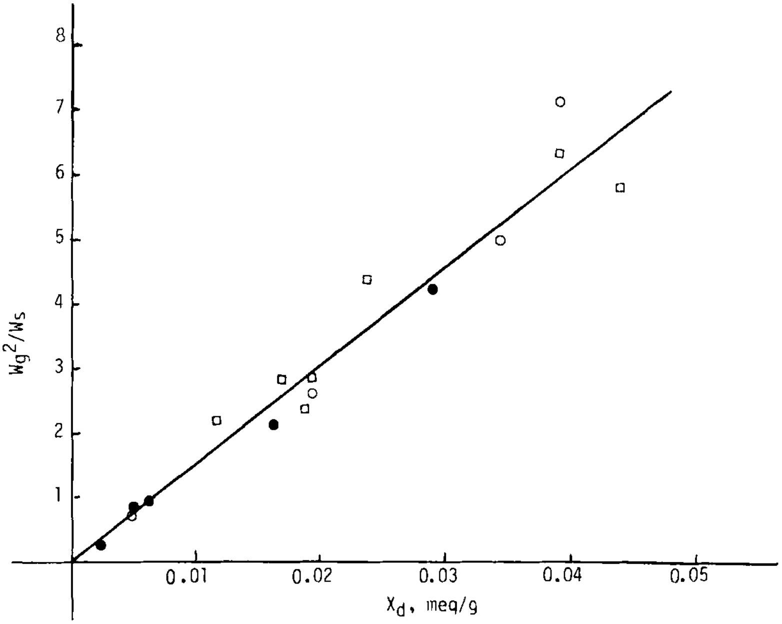

FIG. 5. Variation of crosslink density with W_g^2/W_s: (○) variation in cure, Butarez CTL-II; (●) variation in cure, Hycar CTBN; (□) fully cured, Butarez CTL-I and CTL-II; (—) $X_d = 0.0065\ W_g^2/W_s$.

The derivation of the Flory and Scanlan relations is general and should hold regardless of the nature of the polymer. The Charlesby equation was derived by considering random chain scission and crosslinking of a polymer having a most probable or random molecular weight distribution, and the number-average molecular weight before crosslinking entered the final equation. However, in the present case, we are considering polymer networks built up by stepwise or condensation polymerization without chain scission and the initial molecular weight should enter only as it effects the crosslink density.

The precision to be expected from the use of Eqs. (3), (6), (10), and (13) can be measured by the coefficient of variation of the proportionality constants of the equations as determined by the same sets of data. Table 6 shows that the Flory-Miller, Macosko constant for 14 sets of data has a coefficient of variation of 20.1%, the Charlesby constant, 17.4%, the Scanlan constant, 14.4%, and the constant in

TABLE 6. Comparison of the Constants in the Crosslink Density-Gel Content Relations

Stocks (cure time)	X_d (meq/g)	W_g	W_s	C, Eq. (3)[a]	k, Eq. (6)[b]	b, Eq. (10)[c]	K, Eq. (13)[d]
Series A							
12.5	0.00506	0.578	0.422	0.560	0.0101	0.203	0.00641
16	0.0192	0.776	0.224	0.407	0.0132	0.170	0.00738
23	0.0347	0.855	0.145	0.379	0.0145	0.171	0.00694
61	0.0393	0.890	0.110	0.312	0.0125	0.148	0.00546
Series B							
6	0.0025	0.411	0.588				
6.5	0.00498	0.588	0.412	0.504	0.0094	0.184	0.00593
7.5	0.00615	0.617	0.383	0.485	0.0100	0.180	0.00621
14	0.0164	0.743	0.257	0.457	0.0136	0.184	0.00763
23	0.0285	0.837	0.163	0.364	0.0135	0.162	0.00667
Fully Cured							
	0.0116	0.750	0.250	0.309	0.0094	0.124	0.00520
	0.0189	0.752	0.248	0.486	0.0149	0.198	0.00825
	0.0191	0.784	0.216	0.383	0.0126	0.160	0.00674
	0.0169	0.786	0.214	0.329	0.0109	0.139	0.00583
	0.0391	0.878	0.122	0.348	0.0137	0.162	0.00619
	0.0443	0.871	0.129	0.420	0.0164	0.193	0.00753
	0.0236	0.840	0.160	0.295	0.0109	0.130	0.00535

Sum	6.038	0.1856	2.508	0.09772
Mean, (meq/g)	0.403	0.0124	0.167	0.00651
σ	0.081	0.0022	0.024	0.00091
Coefficient of variation	0.201	0.174	0.144	0.139

[a] C: Flory-Miller, Macosko [1, 13].

[b] k: Charlesby [3-5].

[c] b: Scanlan [6, 7].

[d] K: this paper.

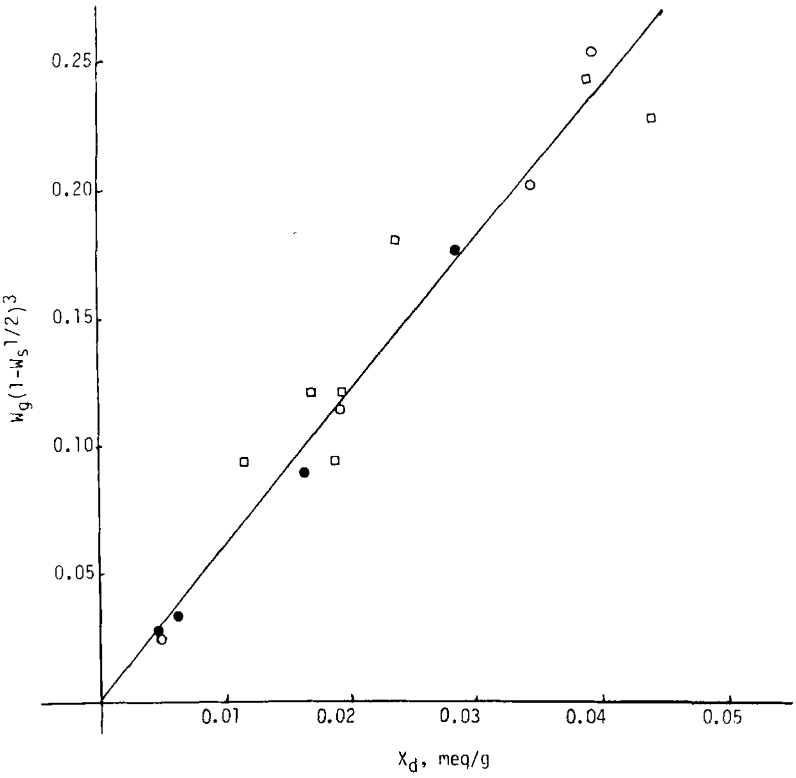

FIG. 6. Crosslink density versus Scanlon function: (○) variation in cure, Butarez CTL-II; (●) variation in cure, Hycar CTBN; (□) fully cured, Butarez CTL-I and CTL-II; (—) $X_d = 0.167\ W_g(1 - W_s^{1/2})^3$.

Eq. (13), 13.9%. In view of the simple form of Eq. (13) and (14), as compared with Eqs. (3), (6), and (10), and the known improper form of Eq. (2), use of Eqs. (13) and (14) would seem to be preferred.

Equation (13) may be further tested by means of equilibrium solvent swelling. Flory [1] derived an approximate relation connecting solvent swelling with crosslink density for lightly crosslinked samples:

$$X_g = 2(0.5 - \mu)V_2^{5/3}/F\rho V_1 \qquad (17)$$

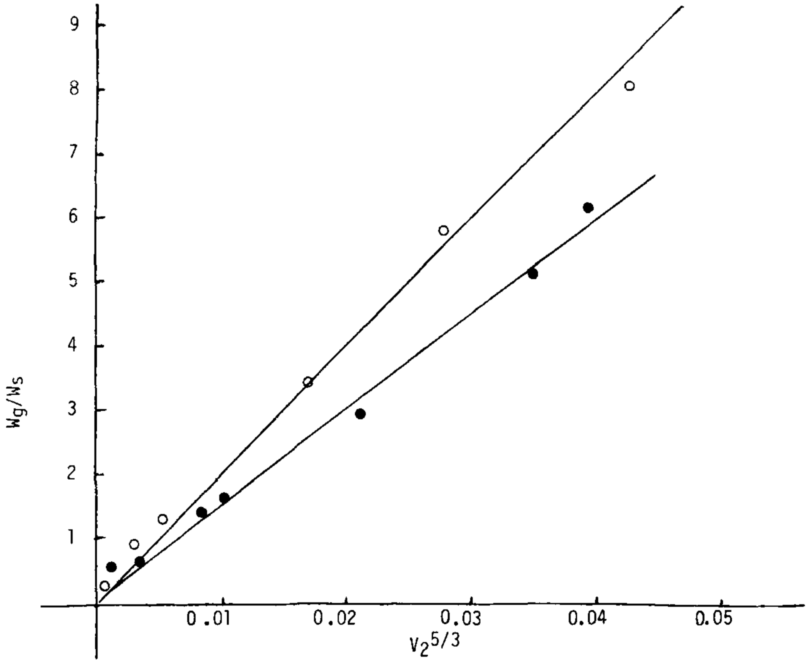

FIG. 7. Plots of W_g/W_s versus $V_2^{5/3}$: (○) series A; (●) series B.

where V_2 is the volume fraction of polymer in the solvent swollen gel, μ is the polymer-solvent interaction parameter, F is the number of chain segments united at branch points, X_g is the concentration of branch points/g in the gel (mole/g), ρ is polymer density, and V_1 is the molar volume of solvent. Combining Eqs. (13) and (17) yields

$$W_g/W_s = 2(0.5 - \mu)V_2^{5/3}/KF\rho V_1 \tag{18}$$

Figure 7 shows that W_g/W_s is a linear function of $V_2^{5/3}$. From the slopes and a knowledge of K, the polymer-solvent interaction parameters may be calculated. However, more accurate values can be obtained from the complete Flory-Huggins equation which may be put in the form:

TABLE 7. Relations Connecting Sol Content, Extent of Reaction, and Crosslink Density

Equation	Source	Equation connects[a]	Proportionality constant (meq/g)	Coefficient of Variation (%)[b]	Remarks
2	Flory [1]	e_g–W_s	–	–	Gel content too low; each case requires a separate equation.
3	Miller and Macosko [13]	X_d–W_s	0.403	20.1	
8	Charlesby, French [3, 4, 16]	e_g–W_s			
6	Charlesby [3, 4]	X_d–W_s	0.0124	17.4	
9	Scanlan [6, 7]	e_g–W_s			Gel content too low; each case requires a separate equation.
10	Scanlan [6, 7]	X_d–W_s	0.167	14.4	
14	French [this paper]	e_g–W_s			
13	French [this paper]	X_d–W_s	0.0065	13.9	

[a] e_g = extent of reaction in gel; W_s = weight fraction of sol; X_d = crosslink density.
[b] Coefficient of variation of the proportionality constant from 14 sets of data.

$$\mu = \frac{-\ln(1 - V_2)}{V_2^{2}} - \frac{1}{V_2} - \frac{X_g F\rho V_1}{2V_2^{5/3}} \qquad (19)$$

Equation (19) yields a value of μ of 0.29 for carboxy-terminated polybutadiene (series A stocks) in xylene and of 0.39 for the carboxyl-terminated butadiene-10% acrylonitrile copolymer (series B stocks), also in xylene with no measurable variation with crosslink density.

CONCLUSIONS

It is concluded that crosslink densities of polymeric stocks may be calculated from values of the gel content based on the reactive portion of the stock, that is, exclusive of plasticizers and fillers. Where entanglements may be neglected, the crosslink density is directly proportional to a function of the gel and sol contents. However, the search for these functions resulted in an embarrassment of riches. Four equations were found or developed. Without going into the derivations of these equations, they can be discussed with reference to their precision and applicability. (Table 7). For condensation polymers, the relations may be modified to enable calculation of the gel content at any degree of reaction in the gel.

In regard to the relations between extent of reaction and the sol content in a stepwise polymerization, experimental data are not available for partially cured samples but some results are available for fully cured stocks whose maximum extent of reaction can be estimated [18]. The stock used in Fig. 1 will have a maximum extent of reaction of no more than 0.89 with an 85% gel content, while a similar prepolymer cured with an isocyanate of functionality averaging 2.5 will have a maximum possible extent of reaction of 0.81 and a 97.5% gel content. These values eliminate Eqs. (9) (Scanlan) and (2) (Flory) from consideration, since these equations predict 72% gel at 0.89 extent of reaction and 94% gel at 0.81 extent of reaction, respectively. Furthermore, both of these equations are derived for particular cases and each new case requires separate solutions. Equations (8) and (14) adequately predict the course of development of the gel as far as is known from present information.

Considering relations relating sol content and crosslink density, the real criterion is not theoretical foundation but whether the result is accurate. Best precision is obtained by Eq. (13), followed closely by Eq. (10) (Scanlan) which, however, derives from considerations which lead to the erroneous Eq. (9).

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