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# Scaling relations in weak and late cross-linked polymers

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## Abstract

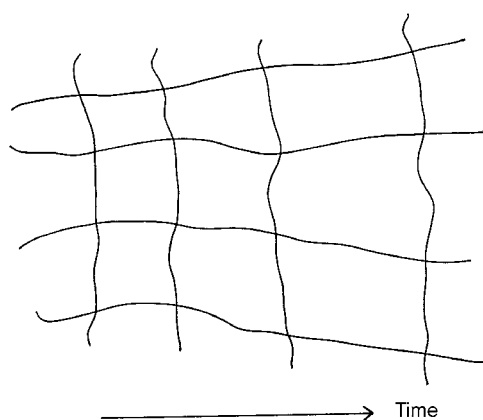
The mechanical properties of polymer network structures depend mostly on the network rigidity. In very weakly cross-linked systems, entanglements also play a predominant role in the mechanical properties, especially hardness; and the contribution of entanglements competes with the contribution of the network rigidity. The entanglement and the network rigidity both depend on chain length and its distribution. In this work, the chain length distribution was affected by adding the cross-linker in late periods. The chain distribution was expressed by a mathematical equation using probabilistic concepts. Hardness was expressed in terms of a chain distribution probability function. It was modified to include the effect of the chain alignment for the polymers that have alignment. It was found that scaling relations existed between (i) the cross-linker concentration 'C', (ii) the molecular weight of the prepolymer that gives the maximum hardness ( $MW_{\max}$ ), (iii) a parameter 'k' that appears in the mathematical equation, and (iv) a parameter 'g' that shows the contribution of chain alignment to hardness. Combined scalings with simple numerical powers were also found among these parameters. The combined scaling  $k \times MW_{\max} \sim C^{-1}$  holds true for both polymethyl methacrylate and polystyrene. It seems to be a universal relation.

## 1. Introduction

The physical properties of polymers, such as the glass transition temperature, dynamic mechanical properties, and conductivity, and the mechanical features, such as stress–strain properties in tension, fatigue, toughness, impact, and hardness, depend on the chemical structure of the polymer, molecular weight, and crystallinity.

The molecular weight (MW) plays a predominant role in the physical and mechanical properties of polymers. Although paraffin and polyethylene have similar chemical structures,

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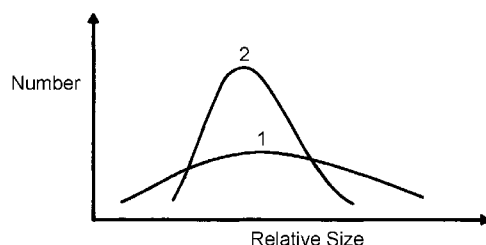
**Figure 1.** Change of sizes of loops during polymerization.

their physical and mechanical properties are not comparable because their molecular weights are very different; one is an oligomer and the other a polymer. The chain entanglement in large molecules changes the properties to a large extent. The chain entanglement increases with the increase of MW and it reaches a limiting (or saturation) value at a critical value of the MW. In network polymers the physical and mechanical properties are mainly controlled by network rigidity—that is, by the extent of cross-linking. The rigidity of the network increases as the amount of cross-linker increases, because the lengths of chains between two cross-linking sites decreases, imparting higher rigidity to the network.

In linear polymers the entanglement can be realized as physical cross-linking. The heavy entanglement decreases the chain length between two entanglement sites resulting in a rigid structure, and it improves the physical and mechanical properties. The physical entanglement and the chemical cross-linking impart similar behaviour in linear and network polymers respectively. The addition of significant amounts of cross-linker results in short chain lengths between cross-linking sites and essentially removes all entanglements. So, the cross-linking removes the contributions of entanglement but introduces network rigidity. If the amount of cross-linker is very low, then we may see both entanglement and cross-linking in the polymer, and the physical and mechanical properties of the polymer become dependent on the joint effects of entanglement and cross-linking. However, physical entanglement and chemical cross-linking are competitive in such a polymer; one increases while the other decreases. This is a typical situation seen in nonlinear growth or chaos theories where one of the competitive parameters increases while the other decreases during growth [1–5]. The growth then results in a scaled change in some of the properties of the system. The scaled change in the parameters of a polymer network system can be highly affected by the cross-linker density. However, in order to influence the chain length between two cross-linking sites, the cross-linker needs to be added at late periods, because, this will provide a much better control on the length distributions of chains in the network.

In radical polymerization the monomer and the cross-linker usually have different reactivities. If the cross-linker is more reactive than the monomer, it is used up faster than the monomer, and the loops formed in the network get larger in size in later periods as seen in figure 1.

The large loops formed in late periods decrease network rigidity while the entanglements tend to increase the rigidity of the polymer.



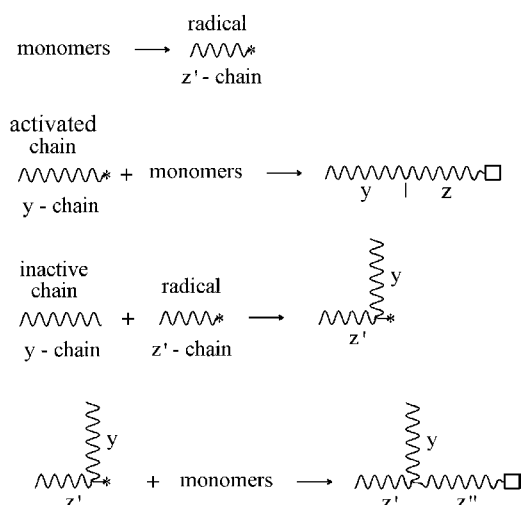
**Figure 2.** Distribution of loops; (1) for very early and very late addition of the cross-linker; (2) for late addition of the cross-linker.

Another important factor is that the chain termination due to disproportionation results in two chains; one dead, and the other inactive with a vinyl group at the end. The latter can be reactivated and it then gives a linear or branched polymer with increased chain length. Therefore the late addition of the cross-linker increases the probability of reactions that yield longer chains, which, in turn, results in loops with larger sizes. In other words, the small-sized loops of the network decrease on late addition of the cross-linker, and the sizes of loops become more uniform with a narrower distribution. However, upon very late addition of the cross-linker the chains become quite immobile and the cross-linker usually reacts with easily diffusing monomers, so the size distribution again becomes broadened. So, the large-size vinyl-terminated chains result in large loops, and the increased fraction of cross-linker to vinyl-group-carrying monomer plus inactive chains gets greatly increased for very late addition of the cross-linker. The very late addition of the cross-linker also yields large loops, like the very early addition. In between, loops emerge with more uniform sizes. This is seen in figure 2.

The change of the sizes of the loops, and thus the associated change of the physical properties, of the polymer network can be related to the length distribution of chains among cross-linking sites. There is no way to measure the length of these chains. However, we can find a mathematical relation between the lengths of the chains just at the time of the addition of the cross-linker (e.g. of prepolymer) and the lengths of chains between cross-linking sites in the network. The change in the physical and the mechanical properties can then be related to the chain length (i.e. MW) for the prepolymer.

In this research the changes in hardness of polymethyl methacrylate and polystyrene network polymers with respect to MW for the prepolymer were studied, and scaling relations were investigated.

Hardness is the ability of a body to withstand the introduction of foreign bodies into its surface layers. Hardness combines concepts of resistance to penetration, scratching, marring, and so on; therefore it is a composite property. Hardness tests are usually based on resistance to penetration by an indenter pressed into the polymer under a constant load. Hardness is the resistance to permanent indentation, but the shape of the tool used to produce the indentation significantly affects the resistance. A hardness number is a highly complex value, which includes the summation of a number of basic properties in proportions dependent on the shape of the indenting tool. The elastic properties of materials determine their resistance to indentation. When an indenter with dynamic energy strikes a surface, elastic and perhaps plastic indentation is produced and, thus, work is done. The elastic recovery generally results in a rebound of the indenter when deformation is completed. The affected atoms tend to return to their original positions. The chemical structure and the extent of entanglement in linear polymers, and the extent of cross-linking in network polymers are predominant parameters in the hardness of amorphous polymers. In semicrystalline polymers, the degree of crystallinity



**Figure 3.** Possible reactions of radical polymerization (the small square represents the cross-linker).

and the structural arrangement of hard crystalline and amorphous regions play important roles in the surface microhardness. In melt-crystallized polymers the local deformation of the lamellar structure is measured by a microindentation hardness test. The materials with thin and less perfect crystals are indented easily. Hardness testing has been applied to different polymers to study structure–property relationships [6–15].

## 2. Mathematical modelling

We consider a polymerization medium where initiator, monomer, dead chains and vinyl-terminated inactive chains coexist. Let us consider a vinyl-terminated chain carrying  $y$  monomer units on its backbone, and call it a  $y$ -chain. Before the late addition of the cross-linker, the  $y$ -chains show a distribution [16]. The chains formed after the addition of the cross-linker will be called  $z$ -unit chains. Figure 3 shows the possible reactions taking place in the medium.

In the first case, monomer molecules react with each other to give a radical of the  $z'$ -unit. A second reaction takes place between an activated  $y$ -chain, which is activated by some means such as a chain-transfer mechanism, and monomer molecules yielding a chain ( $y + z$ )-unit chain. It then interacts with a cross-linker molecule. A third reaction is between an inactive  $y$ -chain and a radical of the  $z'$ -unit. Growth is continued by the addition of  $z''$  new units, and then there is reaction with a cross-linker molecule as seen in the last step of figure 3. We can let  $z' + z'' = z$  here.

Let  $C$  be the mole fraction of the cross-linker added. The probability of a chain interacting with another monomer is proportional to  $(1 - C)$ . The probability for the  $y$ -chain to achieve  $z$  new units in its backbone is  $(1 - C)^z$ . The probability that the chain now interacts with a cross-linker molecule is  $(1 - C)^z C$ . Although four arms emanate from a cross-linker, it actually contains two main chains, each main chain passing through a functional group of the cross-linker. So the probability that two chains have lengths with  $z_1$  and  $z_2$  units, respectively, is given by

$$P = (1 - C)^{z_1} (1 - C)^{z_2} C^2. \quad (1)$$

After the addition of the cross-linker,  $z_1$  and  $z_2$  monomers combine with  $y_1$  and  $y_2$  chains respectively. The total number of monomers on the linear chain is denoted by  $x$ , and  $x_1$  and  $x_2$  are the monomers on chains 1 and 2 respectively. Then, one can write

$$y_1 + z_1 = x_1 \quad (2)$$

$$y_2 + z_2 = x_2. \quad (3)$$

Thus,

$$(y_1 + z_1) + (y_2 + z_2) = x_1 + x_2 = x \quad (4)$$

where  $x$  is the number of monomer units formed on the linear chain overall.

In all types of polymerization, the lengths of polymer chains show certain statistics. The lengths of chains present in the medium just before the addition of the cross-linker show a distribution, which can be expressed by a probability distribution function. The lengths of chains achieved after the addition of the cross-linker also show a similar distribution. That is, both  $y$ -chains and  $(y + z)$ -chains exhibit distribution. When the number of  $y$ -chains versus  $y$ -chain length and the number of  $z$ -chains versus  $z$ -chain length are plotted, an asymmetric curve can be obtained in each case [16]. This chain length distribution function can be identified by its most probable (i.e. maximum) and average values, as in the case of asymmetric distributions. Therefore, both  $y$ -chains and  $z$ -chains can be described separately by similar functions with different maximum and average values. So, one distribution can be related to the other by taking the ratio of their maximum values. The molecular weights of these chains are expected to change by some constant factor. Therefore,  $y$  and  $z$  can be related by

$$y_1 = k_1 z_1. \quad (5)$$

Similarly,

$$y_2 = k_2 z_2. \quad (6)$$

The coefficients  $k_1$  and  $k_2$  in equations (5) and (6) correspond to the effect of cross-linker concentration on the chain. As the concentration of cross-linker increases,  $z/y$  decreases. One can also relate  $x_1$  and  $x_2$  by

$$x_1 = k_3 x_2 \quad (7)$$

where  $k_3$  is the ratio of the  $x$ -type monomers combined in chains 1 and 2, and this ratio is not dependent on the cross-linker concentration. When equations (6) and (7) are substituted into (5) and (6) respectively, the following relations are obtained:

$$k_1 z_1 + z_1 = x_1 \quad (8)$$

$$k_2 z_2 + z_2 = x_2. \quad (9)$$

Therefore,

$$z_1 = \frac{x_1}{(1 + k_1)}, \quad z_2 = \frac{x_2}{(1 + k_2)}. \quad (10)$$

The sum of  $z_1$  and  $z_2$  is the number of total monomers that are added to the chains just after cross-linker addition:

$$z_1 + z_2 = \frac{x_1}{(1 + k_1)} + \frac{x_2}{(1 + k_2)}. \quad (11)$$

When equation (7) is substituted in (11), one gets

$$z_1 + z_2 = \frac{k_3 x_2}{(1 + k_1)} + \frac{x_2}{(1 + k_2)}. \quad (12)$$

Thus,

$$z_1 + z_2 = x_2 \left[ \frac{k_3}{(1+k_1)} + \frac{1}{(1+k_2)} \right]. \quad (13)$$

It is clear that  $x_1 + x_2 = k_3 x_2 + x_2 = x_2(1+k_3)$ . The substitution of this relation in equation (4) gives

$$x_2 = \frac{x}{(1+k_3)}. \quad (14)$$

When equation (14) is substituted into (13),

$$z_1 + z_2 = \frac{x}{(1+k_3)} \left[ \frac{k_3}{(1+k_1)} + \frac{1}{(1+k_2)} \right] \quad (15)$$

$$z_1 + z_2 = k'x \quad (16)$$

where

$$k' = \frac{1}{(1+k_3)} \left[ \frac{k_3}{(1+k_1)} + \frac{1}{(1+k_2)} \right]. \quad (17)$$

In equation (16), two branches of the cross-linker are considered without including the cross-linker molecule. To express  $z$  in terms of the number of linkages we need to write equation (16) as

$$z_1 + z_2 = k'x - 2. \quad (18)$$

Each chain has one less linkage than the total number of monomers on the chain. So, '2' must be subtracted for two chains.

Equation (1) can be written in shortened form as

$$P = (1 - C)^{z_1+z_2} C. \quad (19)$$

When equation (18) is substituted in (19), one gets

$$P = (1 - C)^{k'x-2} C^2. \quad (20)$$

The product of equation (20) and the number of combinations of values of  $z$  that fulfil equation (18) gives the probability that  $k'x$  units distribute over two linear chains emanating from the cross-linker. Therefore,

$$P \sim \left[ \frac{(k'x)!}{(k'x-2)!} \right] (1 - C)^{k'x-2} C^2. \quad (21)$$

Equation (21) is the total probability that a chain can interact with both monomer and cross-linker.

The factor  $(k'x)!/(k'x-2)!$  is the permutation showing in how many ways the cross-linker and the monomer can interact with the chain. It denotes the probabilities of the arrangements of monomer molecules and cross-linker on the chain.

Rearranging equation (21) gives

$$P \sim (k'x)(k'x-1)(1 - C)^{k'x-2} C^2. \quad (22)$$

Equation (22) is expressed in terms of  $x$ , which is the number of monomer units on linear chains just before the addition of the cross-linker. We note that  $x$  includes  $z$ , which cannot be determined experimentally. We need to express it in terms of something that can be experimentally determined. The substitution of equation (16) in (4) gives

$$y_1 + y_2 = x - (z_1 + z_2) = x - k'x = x(1 - k') = k''x. \quad (23)$$

In these equations  $y$  (or  $y_1, y_2$ ) denotes the chain length of the prepolymer just before the addition of the cross-linker and it can be determined experimentally. It can be related to the MW  $M$ , such that,  $y = k''x = k'''M$ ; and so,

$$k'x = k' \frac{y}{k''} = \frac{k'k'''}{k''} M = kM. \quad (24)$$

Thus, equation (22), becomes

$$P \sim (kM)(kM - 1)(1 - C)^{kM-2} C^2. \quad (25)$$

The change of hardness with the prepolymer MW can be given by multiplying equation (25) by a constant coefficient  $h$  that has the physical unit of hardness. If  $h_0$  denotes the hardness of the polymer network for the case where the cross-linker is introduced into the reaction medium just at the beginning of the polymerization process, then the hardness of the late cross-linked polymer will be

$$H = h_0 + hkM(kM - 1)(1 - C)^{kM-2} C^2 \quad (26)$$

where  $H$  shows the hardness of the polymer network. The second term is the contribution due to distribution changed in late cross-linking.

Equation (25) expresses the probability distribution function of the chain lengths between cross-linking sites. According to statistical mechanics it has the information content of  $I = K \log P$  (i.e. the Shannon entropy), where  $I$  is the information content and  $K$  is a constant. In equation (26),  $h$  is a constant that converts the information of the way in which chains are distributed into hardness. The mechanisms of polymerization before and after the addition of cross-linker are the same. An inactive linear chain may form even after the addition of the cross-linker. It may then be reactivated by some mechanism, so it adds some new monomers and then a cross-linker. For this case we have to reinterpret the meanings of 'y' and 'z'; 'y' represents the inactive chain already available, and 'z' the units added after y is activated. The probability function derived under these conditions will be of the same form as equation (25).

Equation (26) shows the relation between hardness, which is a macroscopic property, and some molecular properties like the cross-linker mole fraction, the MW of prepolymer, and its distribution. Equation (26) is valid only for amorphous polymers. Hardness changes both with cross-linker concentration and with crystallinity. The segment length distribution has a direct effect on the crystallinity. In other words, in weakly cross-linked systems, crystallinity is controlled by the chain statistics of segments. Thus, the contribution of crystallinity to hardness can be expressed by

$$\Delta H \propto P\rho \quad (27)$$

where  $\rho$  is the percentage of crystallinity determined experimentally. On introducing a constant  $g$  into equation (27), it becomes

$$H = gP\rho. \quad (28)$$

Importing this relation to equation (26) gives

$$H = h_0 + h(1 + g\rho)kM(kM - 1)(1 - C)^{kM-2} C^2. \quad (29)$$

This equation states that in a late cross-linked system, the hardness of the polymer depends on three factors, which are: (i) the cross-linker mole fraction, (ii) the MW of the prepolymer, and (iii) the degree of crystallinity. In the case of amorphous polymers, the factor  $(1 + g\rho)$  will be equal to 1, because  $\rho = 0$ .



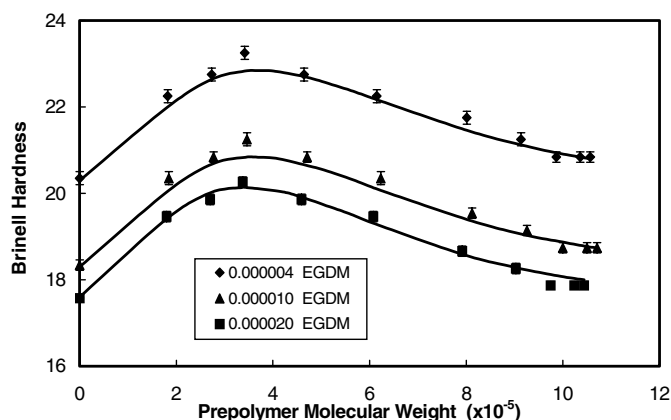


Figure 4. The change of hardness of PMMA with the MW of the prepolymer.

### 3. Experiments

Two different monomers were used in the experiments; one was methyl methacrylate (MMA) and the other styrene (S). The former was cross-linked with ethylene glycol dimethyl methacrylate (EGDM) and the latter with divinyl benzene (DVB). The monomers were purified from their inhibitors, and put into tubes together with 0.5% dibenzoyl peroxide used as initiator. The tubes were closed and immersed into a constant-temperature water bath. MMA was polymerized at 50 °C while S was polymerized at 60 °C. Three millilitres of prepolymer solution was taken from the tubes just before the addition of the cross-linker, and weight-average molecular weights of the prepolymers were determined by viscometric methods and also utilizing the constants given in [17, 18]. The cross-linker mole percentages used for MMA were  $0.4 \times 10^{-3}$ ,  $1 \times 10^{-3}$ , and  $2 \times 10^{-3}$ , and for styrene  $0.66 \times 10^{-4}$ ,  $2.2 \times 10^{-4}$ ,  $4.4 \times 10^{-4}$ , and  $5.5 \times 10^{-4}$ . We need to use such low concentrations in order to investigate the effect of chain statistics in relation to the competitive effects of entanglement and network rigidity, and thus to investigate the resulting scaling behaviour of the network.

The tubes were kept in the water bath for one day. The glass tubes were then removed and the solid polymers were kept in an oven at 70 °C for another day, and under vacuum at 80 °C for one more day. Hardness tests were carried by using (i) the Brinell hardness method (ISO 2039-73) (Instrument: Heckert HPO 250–CMEA PC 501-66), and (ii) a Shore D (ASTM D2240) durometer. The two techniques yield similar results.

### 4. Results and discussions

#### 4.1. Hardness

Figure 4 shows the change of hardness of polymethyl methacrylate (PMMA) network polymer.

It is seen from figure 4 that for all three different mole fractions of EGDM, hardness first increases, then passes through a maximum, and then decreases. The addition of the cross-linker at early stages of polymerization results in a rigid network initially, and later a loose network forms with long branches. In very late addition of cross-linker, long chains are formed at the beginning and a rigid network is formed in the last stages of polymerization. Therefore, for very early and very late addition of cross-linker, the polymer contains partially rigid and partially soft zones. Thus, the polymer hardness does not show significant increase since hard zones do not contribute much to hardness in the presence of soft zones. If the cross-linker is added after the linearly polymerized chains have reached certain lengths, the overall rigidity of the network

**Table 1.** The values of the parameters of equation (26) for the PMMA network polymer.

$C$ (mol%)	$h$	$k$	$MW_{\max}$ ( $\times 10^{-5}$ )
0.002	7.1	0.002 095	4.771
0.004	7.1	0.001 161	4.290
0.005	7.1	0.000 973	4.108

increases and it reaches a maximum. This indicates that the hardness is directly dependent on the loop size distribution of the chains between the cross-linking sites—that is, on the chain length (MW) distribution of the prepolymer. The addition of the cross-linker after the formation of chains of a certain size makes a more rigid polymer. The increased rigidity is due to the well distributed cross-links, i.e. the narrow loop size distribution in the polymer. The prepolymer molecular weights that give the maximum hardness are the optimum molecular weights for obtaining the most rigid network structures, which have the narrowest distribution of loop sizes.

In figure 4, all the curves are asymmetric, and as the mole fraction of the cross-linker increases (i.e. from  $0.4 \times 10^{-3}$  to  $2 \times 10^{-3}$ ), the curves shift to the left and downwards. For very low concentrations of the cross-linker, hardness does not always increase with cross-linker concentration, because the loose network rigidity imparted by cross-linking may not be sufficient to compensate for the loss due to disentanglement.

In figure 4 the points are experimental values. The solid curves are obtained from equation (26) by nonlinear regression analysis. There is a very good agreement between the experimental points and the prediction of equation (26).

The values of  $h$  and  $k$  for the curves of figure 4 are given in table 1.

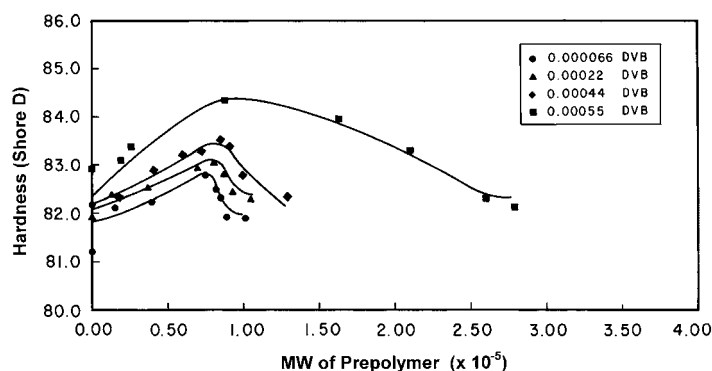
The proportionality constant  $h$  is fixed for all mole fractions of the cross-linker used.  $h$  indicates the coefficient of the contribution of the chain distribution effect to the hardness. The constant value of  $h$  for all cases indicates that the inner structures of the polymer networks for all three cross-linker concentrations in the given range are alike, no matter what the mole fractions of the cross-linker are. In table 1,  $MW_{\max}$  denotes the MW of the prepolymer that gives the maximum hardness. The scaled change in the properties can be based on  $MW_{\max}$ . It stands for the most probable value of the asymmetric curves.

Table 1 shows that the  $k$ -value decreases as the mole fraction of the cross-linker increases. Therefore, it is seen from equation (26) that the effect of the chain distribution on the hardness decreases as  $C$  increases. It must have no significant effect at quite large values of  $C$ .

Figure 5 shows the change of hardness of the polystyrene (PS) network with the MW of the prepolymer.

The curves are asymmetric as in the case of PMMA. As the cross-linker mole fraction decreases, the curves shift to the left and downwards, and get narrower. PS exhibited a different behaviour to PMMA. The x-ray diffraction spectra of PMMA and PS showed that PMMA was purely amorphous while PS had some small degree of crystallinity at some of the concentrations of the cross-linker. The source of the small peaks observed in the x-ray diffraction must be the alignment of the chains. The percentage crystallinity (e.g. chain alignment) is given in table 2.

It is seen from table 2 that chain alignment does not occur at very early (i.e.  $MW = 0.155 \times 10^{-5}$ ) and very late (i.e.  $MW = 1.010 \times 10^{-5}$ ) stages of polymerization. It also did not occur when the cross-linker was added at the very beginning. Very early and very late additions of the cross-linker favour chain entanglement, because there are sufficiently long chains between two cross-linking sites. When the cross-linker is added after the chains have reached certain lengths, the chains become uniform with a narrow size distribution and the number of long chains is decreased. The necessity to occupy a minimum volume forces the chains to make alignments.



**Figure 5.** The change of the hardness of PS with the MW of the prepolymer.

**Table 2.** The percentage alignment in PS at different mole percentages of DVB.

0.000066 (mol%)		0.00022 (mol%)		0.00044 (mol%)		0.00055 (mol%)	
MW ( $\times 10^{-5}$ )	$\rho$ (%)	MW ( $\times 10^{-5}$ )	$\rho$ (%)	MW ( $\times 10^{-5}$ )	$\rho$ (%)	MW ( $\times 10^{-5}$ )	$\rho$ (%)
0.155	0.00	0.133	0.00	0.18	0.00	0.29	0.00
0.395	1.86	0.385	1.65	0.41	7.10	0.51	0.00
0.750	2.10	0.44	3.10	0.60	1.74	0.75	3.90
0.818	0.82	0.49	1.70	0.85	2.69	1.63	3.60
0.850	5.15	0.65	0.40	0.89	3.30	2.60	0.40
0.890	6.50	0.93	7.00	0.95	3.80	2.79	10.85
1.010	0.00	0.99	0.00	1.29	0.00	5.09	0.00

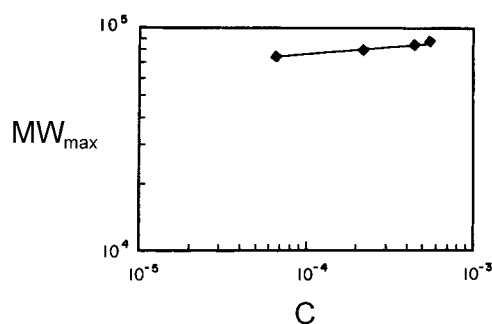
**Table 3.** The values of the parameters of equation (29) for the PS network polymer.

$C$ (mol%)	$h$	$k$	$g$	$MW_{\max}$ ( $\times 10^{-5}$ )
0.000066	1.70	54.73	1.55	0.75
0.00022	1.70	15.35	2.56	0.80
0.00044	1.70	6.920	3.73	0.85
0.00055	1.70	4.670	3.92	0.88

The alignment data given in table 2 were used in equation (29) to allow us to plot its prediction. The solid curves seen in figure 5 are obtained from equation (29) by nonlinear regression analysis. It is seen that there is a very good agreement between the experimental points and the theoretical prediction.

The values of  $h$  and  $k$  for the curves of figure 5 are given in table 3. The  $h$ -value is constant, as it should be, because it is a coefficient relating a certain inner structure to hardness.  $k$  decreases with  $C$  as in the case of PMMA. As  $C$  increases,  $z$  decreases, because vinyl groups of monomers or inactive chains react with the cross-linker molecules more readily. Thus constants  $k_1$  and  $k_2$  of equations (5) and (6) get larger, which, in turn, decreases  $k'$  in equation (17). The decreased  $k'$  gives a larger  $k''$  according to equation (23); hence  $k$  increases, as seen from equation (24).

The value of  $g$  increases as  $C$  increases. This means that the contribution of the chain alignment to the hardness becomes more influential as  $C$  increases. Hardness increases with the increase of the number of hard zones in the structure. As  $C$  increases, chain entanglements decrease, and thus hardness becomes more dependent on chain alignments, which indicate the hard zones in the polymer.



**Figure 6.** The scaling relation between  $MW_{\max}$  and  $C$ .

**Table 4.** The power-law constants for the PMMA network.

Power	$\alpha$	$\beta$	$\gamma$
Value	-0.161	-0.84	5.21

**Table 5.** The power-law constants for the PS network.

Power	$\alpha$	$\beta$	$\gamma$	$\mu$	$\nu$	$\xi$
Value	0.071	-1.140	-5.870	0.430	-14.70	-0.395

#### 4.2. Scaling relations

The change in the distribution of chains between cross-linking sites changes the physical and the mechanical properties of the polymer network. The chain distribution was affected by adding the cross-linker at late times. The parameters of the probability equation affect the hardness in different ways: (i)  $C$  changes the chain lengths between the cross-linking sites overall, (ii)  $MW$  for the prepolymer adjusts the uniformity of the chain lengths, and (iii)  $k$  and  $g$  change with  $C$  and  $MW$ . Therefore, we can expect different scaling relations between the parameters of the probability equation. These relations are expected to be between any two parameters of the probability equation, and they can be in the following forms:

$$MW_{\max} \sim C^{\alpha} \quad (30)$$

$$k \sim C^{\beta} \quad (31)$$

$$k \sim (MW_{\max})^{\gamma} \quad (32)$$

$$g \sim C^{\mu} \quad (33)$$

$$g \sim (MW_{\max})^{\nu} \quad (34)$$

$$g \sim k^{\xi} \quad (35)$$

where  $MW_{\max}$  is the  $MW$  of the prepolymer that gives the maximum hardness. Since the hardness curves are asymmetric, we can use the most probable (i.e.  $MW_{\max}$ )  $MW$  in our scaling relations. These scaling relations can be found by plotting the appropriate parameters of tables 1 and 3 on a log-log scale. The graphs for PS are shown in figures 6–11. Similar graphs were obtained also for PMMA for the parameters  $C$ ,  $MW_{\max}$ , and  $k$ . It is seen from figures 6–11 that in all cases straight lines were obtained, indicating the existence of scalings. The scaling powers of equations (30)–(35) are given in tables 4 and 5.

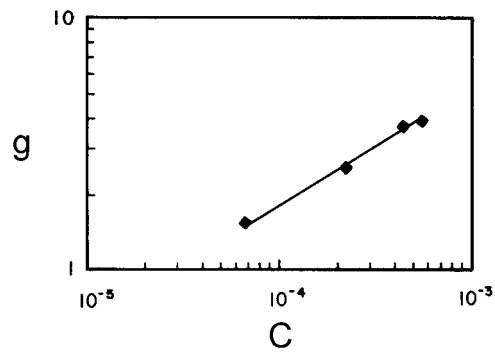


Figure 7. The scaling relation between  $g$  and  $C$ .

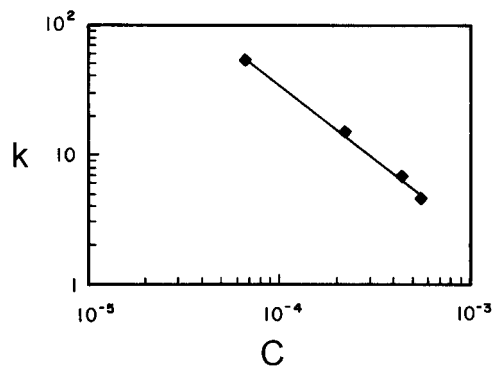


Figure 8. The scaling relation between  $k$  and  $C$ .

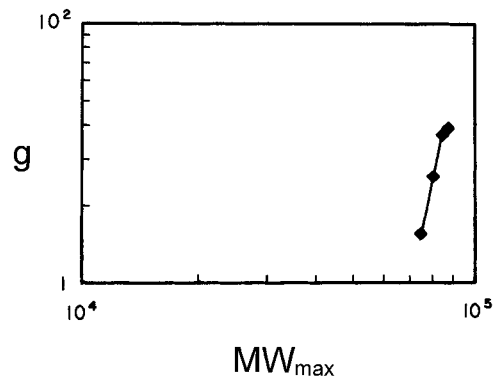


Figure 9. The scaling relation between  $g$  and  $MW_{\max}$ .

An important point is that  $g$ -value appearing in equation (29) looks as if it is an arbitrary constant. The existence of scaling relations between  $g$  and  $C$ ,  $MW_{\max}$ , and  $k$  definitely indicates that it is not an arbitrary constant; it is a system parameter and depends on the other parameters of the network. Another interesting point is that the percentage alignments given in table 2 change arbitrarily depending on the inner structure of the network; however,  $g$  does obey scaling relations.

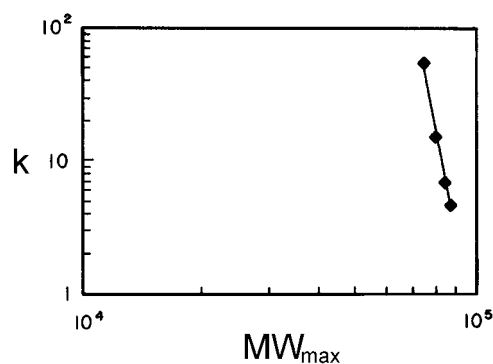


Figure 10. The scaling relation between  $k$  and  $MW_{\max}$ .

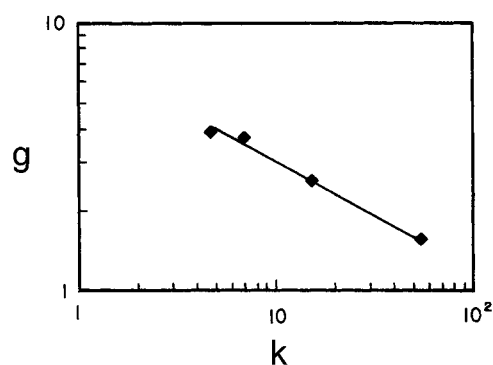


Figure 11. The scaling relation between  $g$  and  $k$ .

#### 4.3. Combined scalings

The existence of scaling relations between all parameters of equations (26) and (29) implies that we can also look for combined scalings among these parameters. The expected relations and their numerical values of powers are as follows.

For PMMA:

$$k MW_{\max} \sim C^{\alpha+\beta} \sim C^{-1} \quad (36)$$

For PS:

$$k MW_{\max} \sim C^{\alpha+\beta} \sim C^{-1} \quad (37)$$

$$g MW_{\max} \sim C^{\alpha+\mu} \sim C^{0.5} \quad (38)$$

$$kg \sim C^{\beta+\mu} \sim C^{-0.7} \quad (39)$$

$$g MW_{\max} \sim k^{\xi+1/\gamma} \sim k^{-0.56} \quad (40)$$

The combined scaling powers are much simpler in the numerical values than the ones of equations (30)–(35), as seen from tables 4 and 5. PMMA does not have chain alignment; therefore, only equation (36) can be considered for it. It is seen from equations (36) and (37) that the scaling  $k MW_{\max} \sim C^{-1}$  holds for both PMMA and PS. It seems to be a universal relation, not depending on the type of polymer.

## 5. Conclusions

- (1) The hardness of weakly and late cross-linked PMMA and PS network polymers changes in an asymmetric form with the MW of the prepolymer.
- (2) It has been found that the theoretical equations (i.e. equations (26) and (29)) describe very well the dependence of hardness on molecular properties such as chain statistics and percentage chain alignment.
- (3) There exist scaling relations between  $C$ ,  $MW_{\max}$ ,  $k$ , and  $g$ .
- (4) Combined scaling relations can be derived from them. The powers of combined relations came out as simple numbers. It was found that,  $k MW_{\max} \sim C^{-1}$ ,  $g MW_{\max} \sim C^{0.5}$ ,  $kg \sim C^{-0.7}$ , and  $g MW_{\max} \sim k^{-0.56}$ .
- (5) The relation  $k MW_{\max} \sim C^{-1}$  holds for both PMMA and PS. It seems to be a universal relation.

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