Chain Interpenetration in Solid Polymer Matrices: A Photochemical Approach

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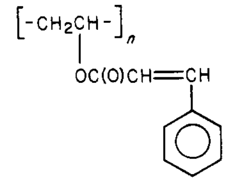
ABSTRACT: In a solid polymer in which cross-links are generated by a bimolecular photoprocess, the extent of interpenetration of the macromolecules may be judged from the relative proportion of intermolecular and intramolecular cross-links produced. If the polymer chains intermingle freely, the likelihood of two adjacent reactant groups belonging to the same chain is small, and intermolecular links will be formed almost exclusively. Intermolecular links increase the molecular weight of the polymer and eventually produce an insoluble gel; intramolecular links have no such effect. Intra- and intermolecular cross-links can therefore be distinguished by their contribution to gel formation. Intermolecular and overall cross-linking efficiencies were determined in films of poly(vinyl cinnamate) and of two photoreactive polyesters based on 4-carboxycinnamic acid and on *p*-phenylenediacrylic acid. The efficiency (Φ) of intermolecular cross-linking was derived from the gel point of the photopolymers, and the overall quantum yield (ϕ) of the photoreaction was estimated from the rate of disappearance of reactant absorption on irradiation. In all three cases, the values of Φ and ϕ were found to be identical within experimental error, indicating a high degree of chain interpenetration in the solid matrix.

The question of chain interpenetration in concentrated solutions of polymers and in solid polymer matrices has attracted some attention in recent years. This interest is due to theoretical,[1] as well as practical, considerations:[2] The micromorphology of polymer chains is an important factor in determining the physical properties of polymeric solids. Braun[3] has written a well-balanced review on the subject, and he concludes that for chemically uniform polymers a considerable degree of coil interpenetration is now generally assumed (see also ref 4 and 5). The most compelling evidence for this comes from experiments with tagged macromolecules embedded in a matrix of the same, untagged, species. Molecular dimensions can then be determined by X-ray[6,7] and neutron scattering[8,9] or by direct observation under an electron microscope,[10] and it is found that the overall volume (radius of gyration) of the tagged molecule is nearly identical with that observed in dilute solution.

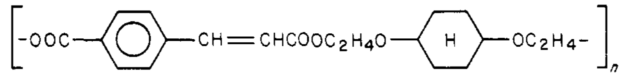
An opposing view, namely that macromolecules interact only at the periphery of their coils and form quasi-cellular structures in concentrated solutions and in amorphous solids, is apparently supported by observations of Vollmert and Stutz[11,12] who monitored the cross-linking reaction between two batches of the same polymer, functionalized with two different, mutually reactive substituents. They found that the reaction did not go to completion but stopped at conversions of less than 20%, and this was interpreted to mean that the inner core of the polymer coils is not involved in the mixing process. To allow for the retarding effect of cross-linking on the rate of coil interpenetration, Vollmert and Stutz varied the degree of functionalization and extrapolated the results of their experiments to the unsubstituted homopolymer. Braun[13a] and Aharoni[13b] have eliminated this questionable procedure by using a single polymer which, after mixing, is made to react by the addition of a diffusible reagent.

Vollmert's, Braun's, and Aharoni's techniques are of necessity confined to solution. We have now found a photochemical method which makes it possible to estimate the extent of coil interpenetration directly in the solid matrix. It is based on the use of a photoreactive polymer in which a cross-linking process can be triggered by an optical signal. An example is poly(vinyl cinnamate) where, on irradiation, cross-links are formed between pairs of cinnamoyl groups.[14] If the macromolecules remain essentially separate in the matrix, most groups in the neighborhood of an excited reactant belong to the same chain, and the majority of photogenerated cross-links will be *intra*molecular. If, on the other hand, the polymer coils interpenetrate freely, the probability that the nearest neighbor of an excited group belongs to the same macromolecule is small, and mainly *inter*molecular cross-links will be formed. The relative efficiency of inter- and intramolecular cross-link formation can therefore be used to estimate the degree of chain interpenetration in the matrix.[13]

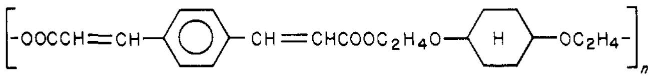
We have investigated inter- and intramolecular cross-linking in the three photoreactive polymers shown here.



I



II



III

In poly(vinyl cinnamate) (I), the photoreactive chromophores are pendant cinnamoyl groups attached to a polyvinyl chain. In polymer II, a similar reactive group is incorporated into the backbone of a polyester. Polymer III is based on the bifunctional chromophore *p*-phenylenediacrylic acid. In all three polymers, cross-links are produced by photocycloaddition between the double bonds of two of the reactant chromophores.[15]

Inter- and Intramolecular Cross-Link Formation

Inter- and intramolecular cross-links can be distinguished by their effect on the insolubilization of the polymer. Intermolecular links increase the molecular weight of the polymer and eventually give rise to a three-dimensional network of chains which constitutes an insoluble gel. Intramolecular links have no effect on molecular weight and do not contribute to gel formation.

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The progress of intermolecular cross-linking may therefore be monitored by the increase in the amount of gel formed during irradiation. A plot of the weight or volume of gel against the radiation dose which produced it is termed the gel curve of the photopolymer.

A point of interest on the gel curve is the minimum radiation dose at which the gel makes its first appearance in the system. This gel point exposure, E_G, is related in a simple way to the quantum yield, Φ, of intermolecular cross-link formation. Consider unit area of an irradiated film of thickness r. If d is the specific gravity of the material and M_0 the molecular weight of the monomer unit, the number of moles of monomer units in the unit area of the film is $(rd)/M_0$, of which the fraction ρ takes part in intermolecular cross-links. The photochemical balance between quanta and cross-links may be expressed in the form

$$EA = rd\rho/M_0 \qquad (1)$$

where E is the incident radiation density (exposure) and A is the fraction absorbed by reactant groups. At the gel point, the cross-link density ρ is given by Stockmayer's rule[16]

$$\rho_G = M_0/M_w \qquad (2)$$

M_w being the weight average molecular weight of the polymer. By combining eq 1 and 2, the relation between Φ and E_G is established,

$$\Phi = rd/E_G A M_w \qquad (3)$$

For an optically thin film, the fraction absorbed may be approximated by

$$A = 2.303\epsilon m_0 r$$

where ϵ is the molar extinction coefficient of the reactant at the wavelength of irradiation and m_0 is its concentration in the solid film. With this, eq 3 takes the form

$$\Phi = d/2.303\epsilon m_0 M_w E_G \qquad (4)$$

If the molecular weight (M_w) of the polymer and the optical characteristics of the film (ϵ, m_0) are known, the quantum yield of *inter*molecular cross-link formation may be obtained from the gel point exposure of the system.

The sum of the inter- and intramolecular cross-links produced by a given exposure is measured by the disappearance of reactant chromophores from the system. The overall quantum yield ϕ of the link-producing photoreaction may thus be derived from the rate of change in the absorption spectrum of the film under irradiation. If I_0 is the incident energy flux (einstein cm^{-2} time^{-1}) and A the fraction absorbed, the rate of change of the optical density D at the wavelength of chromophore absorption may be expressed in the form

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \Delta\epsilon I_0 A \times 10^3 \frac{D - D_\infty}{D}\phi$$

where $\Delta\epsilon$ is the difference in the molar extinction coefficient of reactant and product.

The fraction of intermolecular cross-links produced on irradiation of the polymer film, which is a direct measure of the degree of interpenetration of the macromolecules in the matrix, is given by the quantum yield ratio Φ/ϕ.

Gel Point Exposure

The gel point exposure which is required for the determination of the quantum yield of intermolecular cross-linking may be found by extrapolation of the gel curve to zero gel fraction. However, this procedure puts undue weight on only a few experimental points. A more satisfactory method which makes the whole gel curve contribute to the determination of E_G is based on a theoretical correlation between the amount of gel produced and exposure.

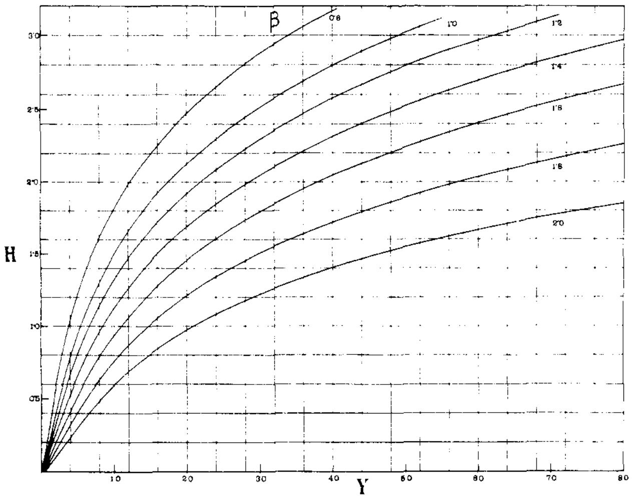


Figure 1. The generalized Flory function $H = F(Y,\beta)$; $H = 2.303\epsilon m_0 h$; $Y = E/E_G - 1$: ϵ, molar extinction coefficient of chromophore; m_0, its molarity in the matrix; h, gel volume in 1 cm^2 of matrix; E, exposure; E_G, gel point exposure; and β, width of molecular weight distribution.

Flory[17] has developed a general equation which relates the weight fraction of gel (W) with the cross-link density (ρ) for *any* primary molecular weight distribution $f(y)$,

$$1 - W = \frac{1}{\sum y f(y)} \sum^{\infty} y f(y)[1 - \rho W]^y \qquad (5)$$

The gel curve is implicit in this expression and may be derived from it, if the molecular weight distribution of the polymer is known. Most current photopolymers have log normal molecular weight distributions, and this is found to be true of polymers I to III. Pitts has numerically integrated[22] the Flory equation using the log normal distribution function[18]

$$f(y)\,\mathrm{d}y = \frac{1}{\beta(2\pi)^{1/2}} \exp\left[-\frac{1}{2\beta^2}(\ln y - \ln y_0)^2\right] \frac{\mathrm{d}y}{y} \qquad (6)$$

where y_0 is the most frequent degree of polymerization and β is the dispersity of the molecular weight distribution. The dispersity β is linked to the molecular weight ratio by the relation $M_w/M_n = \exp(\beta^2)$.

Pitts' results are given graphically in Figure 1. The curves in the diagram represent the dimensionless equation

$$H = F(Y,\beta) \qquad (7)$$

where H is a dimensionless gel volume

$$H = 2.303\epsilon M_0 h \qquad (8)$$

(with h the real gel volume, in cm^3, in unit area of the film), and Y is a dimensionless exposure function

$$Y = \frac{E}{E_G} - 1 \qquad (9)$$

The third dimensionless parameter, β, is the width (dispersity) of the molecular weight distribution. The generalized function $F(Y,\beta)$ describes the progress of gelation *in any photopolymer with a log normal molecular weight distribution.*

The diagram in Figure 1 can now be used to derive E_G from the experimental data. If the dispersity (β) of the

Table I
Polymer Characteristics[a]

	ϵ, L mol^{-1} cm^{-1}	λ, nm	m_0, mol L^{-1}	M_w, g mol^{-1}	β
I	1.10×10^4	300	5.75	2.55×10^5	0.8
II	1.20×10^4	310	2.81	4.9×10^4	1.2
III	1.50×10^4	350	2.59	1.55×10^5	1.4

[a] Molar extinction coefficient (ϵ) and molarity (m_0) of reactive chromophore in matrix, weight average molecular weight (M_w), and dispersity (β) of the molecular weight distribution.

Table II
Gel Point Exposure (E_G), Quantum Yield of Intermolecular Cross-Link Formation (Φ), and Overall Quantum Yield (ϕ) of the Photoreaction

	E_G, einstein cm^{-2}	Φ, mol einstein^{-1}	ϕ, mol einstein^{-1}
I	1.05×10^{-10}	0.26 ± 0.02	0.25 ± 0.02
II	1.01×10^{-10}	0.26 ± 0.02	0.25 ± 0.02
III	3.70×10^{-10}	0.20 ± 0.03	0.22 ± 0.03

polymer is known, e.g., from gel permeation chromatography, the appropriate curve in Figure 1 can be identified, and a value of Y can be found for every point of the experimental gel curve. A plot of $Y(E)$ against exposure is expected to be linear; its slope is the reciprocal of the gel point exposure,

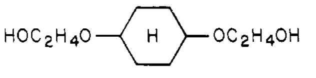
$$dY/dE = 1/E_G \qquad (10)$$

Experimental Section

Materials. The polymers were supplied by the Eastman Kodak Research Laboratories.

Poly(vinyl cinnamate) (I) was prepared by esterification of a medium viscosity grade poly(vinyl alcohol) with cinnamoyl chloride in pyridine. About 15% of the hydroxyls are substituted with acetate groups.

The polyester II was prepared by R. C. McConkey by in-melt condensation of 4-carboxycinnamic acid with the diol



Polymer III was prepared similarly from the same diol and p-phenylenediacrylic acid.[19]

Some of the characteristics of polymers I to III are listed in Table I.

The Gel Curve. Polymer films were coated on quartz plates (50 mm × 50 mm) by solvent evaporation from solutions in dichloroethane (DCE). After the films were air dried, they were annealed for 30 min at 60 °C. Small areas (5 mm × 5 mm) of the films were exposed through the transparent quartz support to monochromatic radiation from a monochromator–xenon lamp combination (Bausch and Lomb, High Intensity Monochromator, Wotan HBX 150 W lamp). A series of exposures was given to about 20 areas on the plate, and the plate was washed in DCE to remove all soluble material. After the plate was dried, the thickness (h) of the gel "images" so formed was measured with a microinterferometer (W. Watson and Sons, Ltd., Barnet, Herts). A plot of the gel volume h against exposure is the gel curve of the photopolymer.

The Overall Photoreaction. For the determination of the overall quantum yield of the cross-linking photoreaction, very thin films (optical density 1.5) were prepared on quartz slides, and their spectra were taken with a Beckmann ACTA VI spectrophotometer. The films were then exposed directly in the spectrophotometer to radiation from the monochromator–xenon lamp unit. The intensity of the exposing beam was determined by ferrioxalate actinometry in situ. Spectra of the irradiated films were recorded at intervals. From a plot of the optical density in the chromophore band against exposure time, the rate of change of optical density (dD/dt) was obtained by numerical derivation.

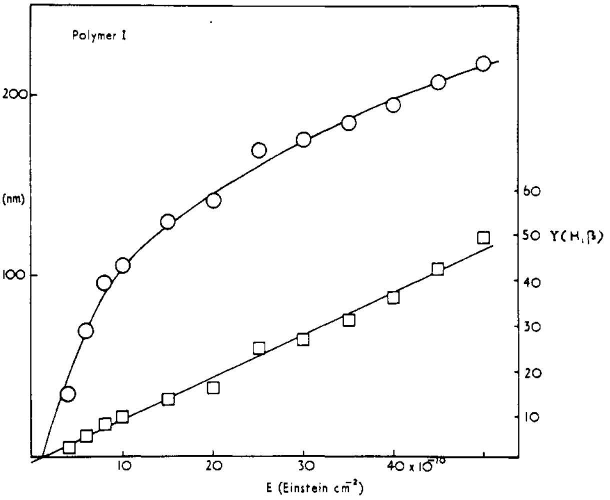


Figure 2. Gel curve $h(E)$ and derived exposure function $Y(E)$ of polymer I exposed to monochromatic radiation of 300 nm.

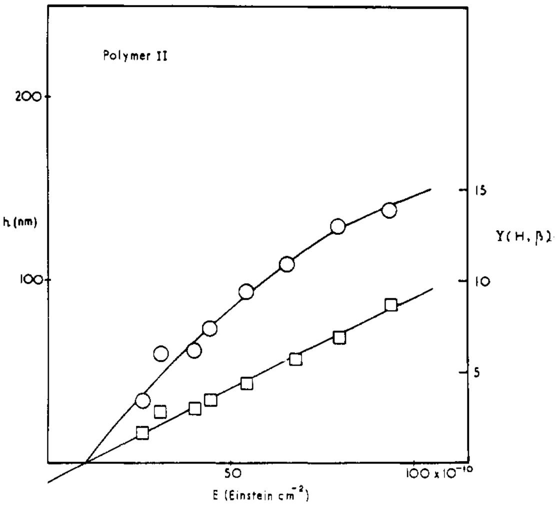


Figure 3. Gel curve $h(E)$ and derived exposure function $Y(E)$ of polymer II exposed to monochromatic radiation of 310 nm.

The overall quantum yield, ϕ, was calculated via eq 6 and extrapolated to zero exposure. The results are listed in Table II.

Ancillary Measurements. Extinction coefficients of the reactant chromophores were determined from solution spectra as well as from the absorption spectra of films of known thickness.

Weight average molecular weights were determined by light scattering photometry on a SOFICA 42000 instrument. Molecular weight and radii of gyration, in DCE solution, were obtained from computer-generated Zimm plots.

The molecular weight distribution of the polymers was determined by gel permeation chromatography, using three AR gel columns of pore sizes 0.3, 1, and 3×10^3 nm, with THF as eluent. Molecular weights were calculated as polystyrene equivalents.

Results

The relevant experimental results are listed in Table II. The gel curves obtained for polymers I to III are shown in Figures 2, 3, and 4, together with the derived exposure functions $Y(E)$. It will be noted that in all three cases the plot of Y vs. E is linear and originates at the point (0,–1), which incidentally justifies the linearization procedure and confirms the correctness of the generalized Flory function in Figure 1. From the graphs in Figures 2 to 4, it can be seen that the uncertainty in the slope $dY/dE = 1/E_G$ is less than ±5% for polymers I and II and not more than ±8% for polymer III.

A measure of the accuracy of the molecular weight determination, which enters the determination of Φ, is

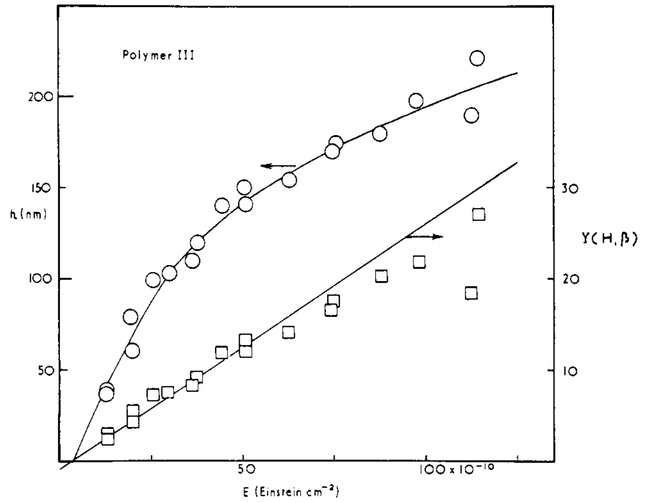


Figure 4. Gel curve $h(E)$ and derived exposure function $Y(E)$ of polymer III exposed to monochromatic radiation of 350 nm.

gained from repeat measurements on polymer II carried out in other laboratories: A light scattering experiment at the National Physical Laboratory in Teddington gave $M_w = 5.2 \times 10^4$ (compared with our value of 4.9×10^4), and a determination of M_n by membrane osmometry (solvent, toluene) at Liverpool University gave $M_n = 1.1 \times 10^4$, which together with the ratio $M_w/M_n = 4.3$ obtained by gel permeation chromatography at Imperial College, London (compared with a value of 4.2 found in this laboratory), leads to a value of $M_w = 4.73 \times 10^4$. These data reflect an uncertainty of less than ±5% in the determination of M_w and lead, for Φ, to the error limits indicated in Table II.

The determination of the overall quantum yield ϕ is more straightforward; however, it involves the gradient of a directly measured quantity ($\mathrm{d}D/\mathrm{d}t$), and its accuracy is therefore not higher than ±8%.

It can be seen from the data in Table II that within the accuracy of the experiment the quantum yield of intermolecular cross-link formation is identical with the overall quantum yield of the cross-link forming reaction: in polymers I, II, and III the formation of intramolecular cross-links, or loops, appears to be negligible. This indicates a high degree of coil interpenetration in the solid matrices of the polymers, in agreement with results of recent neutron scattering experiments,[9] and also in accord with the strongly held views of Flory.[20,21]

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References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.
(2) A. J. Chompff and S. Newman, Eds., "Polymer Networks, Structure and Mechanical Properties", Plenum Press, New York, 1971.
(3) D. Braun, *Angew. Chem., Int. Ed. Engl.*, **15**, 451 (1976).
(4) R. F. Boyer in "Physical Structure of the Amorphous State", G. Allen and S. E. B. Petrie, Eds., Marcel Dekker, New York, 1976, p 253.
(5) W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1 (1974).
(6) W. R. Krigbaum and R. W. Godwin, *J. Chem. Phys.*, **43**, 4523 (1965).
(7) Hyo-Gun Kim, *J. Appl. Polym. Sci.*, **22**, 889 (1978).
(8) D. G. H. Ballard, J. Schelten, and G. D. Wignall, *Eur. Polym. J.*, **9**, 965 (1973).
(9) A. Maconnachie and R. W. Richards, *Polymer*, **19**, 739 (1978), and references therein.
(10) S. M. Aharoni, *Macromolecules*, **11**, 677 (1978).
(11) B. Vollmert and H. Stutz, *Angew. Makromol. Chem.*, **20**, 71 (1971).
(12) B. Vollmert and H. Stutz, *Angew. Makromol. Chem.*, **35**, 75 (1973).
(13) (a) D. Braun and F. J. Quesada Lucas, *Makromol. Chem.*, **142**, 313 (1971); (b) S. M. Aharoni, *Angew. Makromol. Chem.*, **62**, 115 (1977).
(14) F. I. Sonntag and R. Srinivasan, *Tech. Pap., Reg. Tech. Conf., Soc. Plast. Eng., Mid-Hudson Sect.*, 163–170 (1967).
(15) A. Reiser and P. L. Egerton, *Photogr. Sci. Eng.*, to be published.
(16) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).
(17) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 380.
(18) N. J. H. Parham, E. Pitts, and A. Reiser, *Photogr. Sci. Eng.*, **21**, 145 (1977).
(19) Farbenfabricken Bayer A.G., British Patent 838547 (1968).
(20) P. J. Flory, *Macromol. Chem.*, **8**, 1 (1973).
(21) P. J. Flory in "Physical Structure of the Amorphous State", G. Allen and S. E. B. Petrie, Eds., Marcel Dekker, New York, 1976, pp 1–11.
(22) The integration assumes a constant quantum yield of cross-link formation. This is justified in our experiments, since the overall degree of chromophore conversion in the polymer films is low (2–3%).

Properties of Networks Formed by End Linking of Poly(dimethylsiloxane)

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ABSTRACT: Networks with well-defined structures were prepared by end linking vinyl-terminated poly(dimethylsiloxane) chains with tri- and tetrafunctional silanes. Modulus and extent of reaction were followed continuously on several systems. If trapped entanglements are accounted for, the modulus rise can be modeled quantitatively with branching theory. The effect of entanglements is demonstrated by changing molecular weight of the chains and by dilution. Comparison of data between tri- and tetrafunctional cross-linkers indicates clearly the importance of junction mobility. The C_2 Mooney–Rivlin constant is small. Sol fraction and swelling data are also in reasonable agreement with predictions from branching theory.

Most structural information on networks is inferred from some type of elasticity measurement such as swelling or tensile modulus. It is hoped that such data interpreted through rubber elasticity theory will give an accurate measure of the average molecular weight between chemical junctions in the network. With this value and supporting

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