glement, and (iii) the extent of the topological confinement on *cis*-PI due to the surrounding chains (*cis*-PI and the network strands depending on w). The M_e in the infinite dilution state was estimated to be 1700, which is lower than the M_e in pure *cis*-polybutadiene.

(2) The relaxation time of the guest *cis*-PI trapped in BR reduced to the isofriction coefficient state was longer than the bulk *cis*-PI, indicating that the guest *cis*-PI molecules in the network were confined more strongly than in the bulk state.

(3) The relaxation strength of the guest *cis*-PI molecules in BR is smaller than that in the bulk state. This indicates that their mean-square end-to-end distance is smaller than the unperturbed dimension.

Acknowledgment. This work was supported in part by a Grant-in-aid for Scientific Research by the Ministry of Education, Science and Culture (6055062). We also acknowledge financial support and encouragement from the Institute of Polymer Research, Osaka University.

Registry No. PI, 9003-31-0; PB, 9003-17-2.

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Use of Gas Chromatography To Determine the Degree of Cross-Linking of a Polymer Network

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Received June 29, 1988; Revised Manuscript Received December 19, 1988

ABSTRACT: The technique of finite-concentration inverse gas chromatography has been used to estimate the relative cross-link density of ethylene–propylene rubbers that had been cross-linked by using ^{60}Co radiation. The solvent activity in networks swollen with hexane was treated in terms of the Flory–Rehner equation.

Introduction

Over the past two decades, gas chromatography has been used to study a wide range of polymer properties such as glass transition and melting temperatures, crystallinity, and diffusion coefficients.[2,3] In particular, it has been applied to solution studies where measurements of activity coefficients, enthalpies of mixing and of solution, and interaction and solubility parameters may be made rapidly over a wide range of conditions. The purpose of this article is to introduce its use in the characterization of cross-linked polymer networks.

Solutions of linear polymers are usually treated in terms of the Flory–Huggins theory[4,5] for the thermodynamic activity of the solvent, a_1:

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, r is a parameter representing the size ratio of polymer and solvent segments, and χ is the Flory–Huggins interaction parameter which accounts for energetic and noncombinatorial contributions to the free energy of mixing.

Equation 1 was extended to apply to polymer networks by Flory and Rehner,[6] who assumed an additional, additive contribution due to the elastic free energy of deforming the network on swelling with the solvent:

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 + V_1\nu_e/v_2[\phi_2^{1/3} - (\phi_2/2)] \qquad (2)$$

where V_1 and v_2 are the molar volume of solvent and specific volume of polymer. ν_e represents the effective number of cross-links per gram of polymer, i.e., the reciprocal of the molecular weight of the polymer chain between cross-links, M_c.

In characterizing polymer networks, ν_e is usually measured by determining the amount of solvent absorbed in an equilibrium swelling experiment,[7,8] although techniques such as vapor sorption have also been used.[9] There has been considerable debate on the question of the additivity of the various contributions to the free energy of mixing,[10,11] and eq 2 is now recognized to be at best an approximation to the behavior of real systems (much as in the case of the original Flory–Huggins treatment) in that it tends to overestimate the degree of cross-linking. However, despite this, its use remains widespread in polymer chemistry.

Gas chromatography (GC), as usually used to study polymers, often referred to as inverse gas chromatography (IGC), is performed at inifinite dilution of solvent. As long

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ago as 1969, Conder and Purnell[12-15] developed the thory for its use at finite solvent concentrations, but this has received relatively few applications. Brockmeier and coworkers[16,17] measured the activity of a number of polymer solvent systems, and Chang and Bonner[18] found reasonable agreement between chromatographic and vapor sorption results for the polyethylene oxide–benzene mixture. Recently, the elution-on-a-plateau method was used to study solutions of poly(dimethylsiloxane), and agreement with static equilibrium results was shown.[19]

In this work, finite-concentration gas chromatography has been applied to measure the relative degrees of cross-linking of an ethylene–propylene rubber that was cross-linked by using ^{60}CO γ-radiation at various doses.

Theory

The full treatment of the elution-on-a-plateau method has been given by Conder and Purnell[12-15] and by Price and Guillet.[19] It involves the equilibration of the polymer with a stream of inert carrier gas that contains a known concentration of solvent vapor. The retention volume, V_N, of a small amount of solvent injected into the stream is then measured from

$$V_N = (t_r - t_m)F \tag{3}$$

where t_r and t_m are the times taken for the solvent and an inert marker to traverse the column and F is the flow rate of carrier corrected to standard conditions.[20] Under these conditions, it may be shown that the partition isotherm for the solvent between the vapor and solution phases is given by

$$\frac{\partial q}{\partial c} = \frac{jV_N}{v_p(1-\psi)} \tag{4}$$

In eq 4, q and c are the concentrations of solvent in the liquid and vapor phases, respectively, and v_p is the volume of polymer in the column. ψ is the mole fraction of solvent in the vapor stream, corrected by the factor j for gas-phase nonideality and compressibility effects due to the pressure gradient along the column.

Integration of eq 4 and introduction of the weight of polymer in the column, w, allow calculation of the concentration of solvent in the liquid phase, q, expressed as moles per gram of polymer:

$$q = \frac{j}{w}\int_0^c \frac{V_N}{1-\psi}\,dc \tag{5}$$

The concentration in the vapor stream may be calculated from the first terms of a virial expansion:

$$c = \frac{\psi P_A}{jRT + \psi^2 B_{11} P_A} \tag{6}$$

where P_A is the total pressure of carrier gas at the column outlet and B_{11} is the second virial coefficient of the solvent vapor at the column temperature T.

From the definition of q given above, it is clear that the weight fraction of solvent in the solution phase, W_1, is

$$W_1 = qM_1/(1 + qM_1) \tag{7}$$

M_1 being the molecular weight of the solvent. The activity of the solvent in solution may be calculated from the partial pressure of solvent in the carrier stream, P_1, and the saturated vapor pressure of the solvent, P_1^0. Hence, the activity coefficient, Ω_1, may be found:

$$\Omega_1 = a_1/W_1 = P_1/P_1^0 W_1 \tag{8}$$

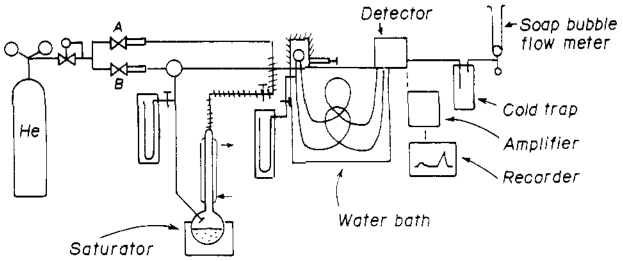

Figure 1. Schematic diagram of finite-concentration gas chromatography apparatus.

It should be noted that in eq 8, Ω_1 represents an activity coefficient rationalized on a weight fraction basis, which is advantageous when dealing with polymer solutions.[21] Thus, having calculated a_1, eq 1 may be applied to find the interaction parameter χ.

Experimental Section

Apparatus. The apparatus used has been described in detail previously,[19] so only a summary will be given here. It is shown schematically in Figure 1.

A known partial pressure of the solvent, n-hexane, was introduced into the helium carrier gas by a saturator consisting of a flask containing n-hexane near its boiling point and a condenser through which thermostated water was passed. Changing the temperature of the water in the saturator condenser allowed variation of the partial pressure of hexane.

The carrier passed over the polymer packing contained in $^1/_4$-in. copper columns as in conventional gas chromatography, then to a thermal conductivity detector, and finally, via a cold trap, to a soap-bubble flow meter for accurate measurement of the carrier flow rate. The columns were contained in an oil bath maintained at 77.0 ± 0.02 °C, measured by using a precision mercury-in-glass thermometer.

After equilibration of the detector at a known concentration of solvent vapor, the retention times of air (the inert marker) and solvent were recorded. An average of at least three values agreeing within 1% was usually taken. Sample sizes of 0.1–0.5 μL were used at low concentrations, although as the concentration became higher, samples of up to 1.5 μL were needed to give an adequate signal.

Materials. Since the saturated vapor pressure of the solvent is required for the calculation of results, solvent purity is of great importance. The n-hexane used was a BDH Assured grade of certificated purity >99.5%. The polymer used was an Aldrich ethylene–propylene rubber copolymer of low average molecular weight and an ethylene content of 70%.

Coating of the polymer onto a solid support of 30–45 mesh size chromosorb P was carried out in the usual manner[20] employing hot toluene as the solvent. The percentage loading was determined by duplicate calcination to be 8.8% after correction for volatiles in the uncoated solid support.[22]

Cross-Linking of Polymers. Approximately 50 g of the polymer coated support was placed in Pyrex glass ampules, and these were evacuated on a glass vacuum line to a pressure of <10^{-5} Torr for 2 days to thoroughly degas the polymers and prevent unwanted degradation reactions. The ampules were then sealed and placed in a ^{60}Co γ-ray source (Gammacell, Atomic Energy of Canada Ltd.). The approximate dose rates were estimated from the activity and known decay rates of the source supplied by the manufacturer. After irradiation, the ampules were broken, and the packing was loaded into the columns in the usual manner.

Solvent Extraction. To gain an independent idea of the cross-linking of the polymers, the irradiated samples were subjected to duplicate Soxhlet extraction with toluene as the solvent. Extraction was carried out for 7 days, followed by an additional 2–3 days to confirm that constant weight has been achieved.

Results and Discussion

The measured solvent retention volumes and vapor mole fractions were used to construct plots of $V_N/(1-\psi)$ versus concentration as suggested by eq 5. The plots are shown in Figure 2. To facilitate the calculation of the solution

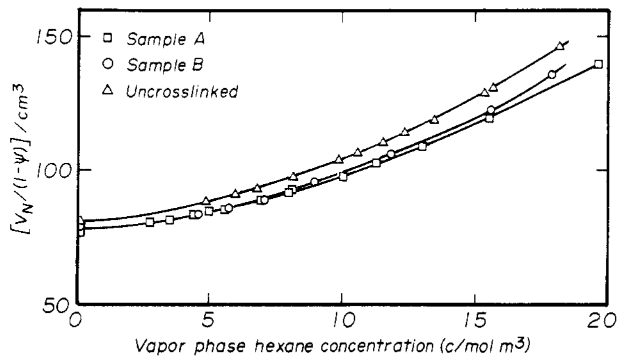

Figure 2. Plot of $V_N/(1 - \psi)$ vs concentration for EPR in n-hexane at 77 °C.

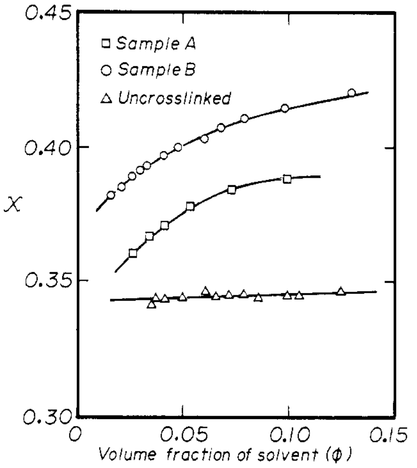

Figure 3. Plots of concentration dependence of interaction parameters for EPR in n-hexane at 77 °C.

composition, the results were fitted to a polynomial expression of the form

$$V_N/(1 - \psi) = a_0 + a_1c + a_2c^2 + a_3c^3 \tag{9}$$

where a_n are constants. The function was then integrated analytically to find q as in eq 5.

In the calculation of the results, a value of 978.02 Torr[23] was used for the saturated vapor pressure of n-hexane at 77.0 °C, -1.250 L mol^{-1} for its second virial coefficient,[24] and 0.6052 g cm^{-3} and 86.178 for the density[25] and molecular weight, respectively. The density of the polymer was taken as 0.8396 g cm^{-3}.[26] It was assumed that the density of the polymer remained unchanged on cross-linking. Gee et al.[9] reported that the density of natural rubber at 30 °C changed from 0.908 to 0.915 g cm^{-3} on cross-linking with dicumyl peroxide. A change of this magnitude in the current work would lead to a change in the solvent volume fraction of ca. 0.001 and hence in χ of ca. 0.003, which is comparable with the experimental error of the method.

The weight fraction of solvent in the liquid phase was calculated from eq 7, and this converted to a volume fraction by using the densities ρ:

$$\phi_1 = \frac{W_1/\rho_1}{(W_1/\rho_1) + (W_2/\rho_2)} \tag{10}$$

The Flory–Huggins interaction parameter was then calculated from

$$\chi = \frac{\ln a_1 - \ln \phi_1 - [1 - (1/r)]\phi_2}{\phi_2^{\,2}} \tag{11}$$

the size ratio being calculated from the ratio of the molar volumes of the polymer and solvent.

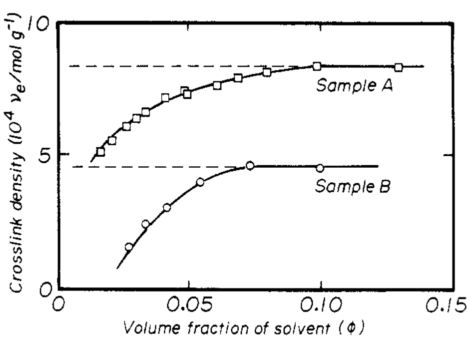

Figure 4. Plot of cross-link density vs concentration for irradiated EPR samples.

Table I
Degree of Cross-Linking for EPR from Finite Concentration Results

sample	radiation dose, Mrad	extractable fraction	$10^4\nu_e$	M_c
A	140	0.68	4.5	2500
B	200	0.75	8.3	1205

The method has been applied to solutions of linear polymers by several workers, who have found good agreement between chromatographic results and those from more conventional techniques such as vapor sorption. A plot of χ versus concentration for the un-cross-linked polymer is shown in Figure 3. As has been shown for a large number of polymer–solvent systems,[27,28] there is a linear variation of χ with volume fraction, although in the present work the increase is small. Linear regression of the results leads to the following equation for χ:

$$\chi = 0.344 + 0.004\phi_1 \tag{12}$$

The value at infinite dilution of solvent, χ^∞, of 0.344 is slightly lower than that of 0.37 interpolated from the work of Ito and Guillet[29] measured directly at infinite dilution. The interaction parameters calculated from the basic Flory–Huggins equation (1) are also shown in Figure 3 and, as would be expected, show a more complex concentration dependence.

For the cross-linked samples, the effective number of cross-links was calculated from the rearranged Flory–Rehner equation (2):

$$\nu_e = v_2\left[\frac{\ln a_1 - \ln \phi_1 - [1 - (1/r)]\phi_2 - \chi\phi_2^{\,2}}{V_1[\phi_2^{\,1/3} - (\phi_2/2)]}\right] \tag{13}$$

the value of χ determined by eq 12. If the Flory–Rehner equation were to hold accurately, ν_e should be independent of concentration. However, Figure 4 clearly shows that this is not the case. The value of ν_e increases with concentration but rapidly reaches a plateau. The most probable explanation for this behavior is that ν_e cannot be determined until the network is fully swollen. The values of ν_e and the molecular weight between cross-links M_c taken from the graphs are shown in Table I. The experimental error of the results is estimated to be 5–8%, leading to errors of 50–200 in the region investigated.

As mentioned earlier, the basic premise of the Flory–Rehner equation, the additivity of the various contributions to the free energy change, has been discussed by several workers, although the results have been conflicting. For instance, Gee et al.[9] and Yen and Eichinger[30] concluded that the elastic and mixing free energies were not separable in this way while the results of Flory and Tatara[10] supported the additivity principle. A number of alternative theories of the swelling of rubberlike networks have been suggested[10,31,32] that contain additional parameters that often have to be treated as adjustments to fit experimental data. In particular, Flory has presented a refined theory that accounts for the way that the cross-links are embedded in the polymer structure. This was not used in the current work since the necessary parameters could not be predicted for this system. However, no single treatment has gained universal application, and the ν_e value from the Flory–Rehner equation remains the most common way of characterizing the cross-link density. Statistical treatment of a random cross-linking process is also possible[34] but requires knowledge of the initial molecular weight and, more importantly, the molecular weight distribution since the resulting equations can be solved only for a very limited number of initial distributions.

The chromatographic method has several advantages over the more usual method of measuring swelling equilibria: (1) There is no need to coat the polymer onto a solid as a ground sample of polymer could be packed directly into the column and the measurements are relatively rapid. This would have the added advantage that the polymers could be swollen in solvent so that the chromatographic results could be directly compared with more conventional techniques, so confirming that our methods would be useful in an absolute manner in addition to yielding relative values as described here. (2) The method involves measurement of the interaction parameter and its concentration dependence, which in most systems is not insignificant. For swelling techniques, these values have to be taken from the literature[35] and are often treated as composition independent.

Conclusions

It has been shown that gas chromatography at finite concentration allows estimation of the relative cross-link density of polymer networks. It has the advantage that it yields additional thermodynamic data for comparison with the predictions of the various theories described above.

It is concluded that the range of applicability of the IGC method can be extended to study insoluble, network polymers in addition to the wide range of systems already amenable to study.

Acknowledgment. The financial support of this work by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. J.E.G. thanks the Canada Council for support in the form of a Killam Research Fellowship.

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