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THE RELATION BETWEEN THE SWELLING OF A NETWORK AND THE INTRINSIC VISCOSITY OF ITS PRECURSOR POLYMER

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ABSRACT

We have established a correlation between the swelling of a network and the intrinsic viscosity of the corresponding linear polymer, by varying the type of solvent. We note that this correlation is not very good and the swelling varies to a greater extent than the intrinsic viscosity.

INTRODUCTION

A dilute polymer solution behaves hydrodynamically as a set of solid spheres with radius R in suspension. According to the Einstein theory, the viscosity η of this solution is given by

$$\eta = \eta_s \left[1 + 2.5\phi\right]$$

where η_s is the viscosity of the solvent and ϕ is the polymer volume concentration

$$\phi = C\,R^3 / N$$

where C is the monomer concentration and N is the polymerization index.

For a given polymerization index, the intrinsic viscosity $[\eta]$ gives the hydrodynamic radius R

$$[\eta] = (\eta - \eta_s) / \eta_s C \simeq R^3/N \qquad (1)$$

For a polymerization index N, the hydrodynamic radius R depends on the polymer-solvent interactions. The end-to-end distance has a square average R_F (1):

$$R_F \sim v^{1/5}\, N^{3/5}$$

where v is the excluded volume parameter characterizing the polymer-solvent interactions. We made a series of experimental measurements of $[\eta]$ for a given polymer in various solvents in order to obtain several values of R.

On the other hand, a gel swollen to equilibrium can be regarded as a solution at overlap threshold, each chain between two crosslinks behaving as in a dilute solution. If the concentration at swelling equilibrium is C^*

$$C^* = N / R_F^3 \qquad (2)$$

If we compare relations (1) and (2) and if we suppose that the hydrodynamic radius is proportional to the end-to-end distance, then we obtain

$$[\eta] \sim C^{*\,-1}$$

If we measure C^* by determining the swelling equilibrium, we obtain proportionality between the swelling of a network and the intrinsic viscosity of its precursor polymer if we vary the polymer-solvent interaction.

EXPERIMENTAL

The networks were made by polycondensation of hydroxytelechelic polyethers, poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO), with toluene diisocyanate (TDI) or a polyisocyanate derived from hexamethylene diisocyanate (BTHI).

	$\bar{M}_n$	functionality	crosslinking reagent
PPO:	= 2500;	= 3;	= TDI
PEO:	4000	2;	BTHI

The intrinsic viscosities were measured on PEO with a mass of 20000 and a bifunctional PPO with a mass of 2000 condensed with the TDI in order to increase its length so that the values of intrinsic viscosity were greater.

The swelling measurements were obtained from the weight variations of a sample immersed in a solvent. The intrinsic viscosity measurements were made on an automatic FICA viscometer. The value of $[\eta]$ (dl/g) was obtained by extrapolation to zero concentration by the classical method. PEO presented problems because of its exceptional ability to crystallize. The PEO network was prepared in solution and so was amorphous. We obtained with many solvents a high swelling value and so we consider them as good solvents. When dissolved in these solvents, the linear PEO often crystallizes after a period. To make these measurements of viscosity, it is necessary either to increase the temperature of the solution or to act very rapidly before the crystallization occurs.

RESULTS

The Tables give the swelling values (ϕ^{-1}) of the networks and the intrinsic viscosities for a series of solvents.

Table 1. Poly(propylene oxide); T = 20°C

solvent	intrinsic viscosity (dl/g)	swelling
diethyl oxalate	* 0.24 ± 0.01	4.96 ± 0.05
dichloromethane	0.39 ± 0.01	10.1 ± 0.1
mesitylene	0.24 ± 0.01	5.3 ± 0.2
1,3-dibromopropane	0.27 ± 0.01	5.50 ± 0.06
o.xylene	0.41 ± 0.01	7.0 ± 0.2
ethyl acetoacetate	0.22 ± 0.01	4.1 ± 0.1
toluene	0.30 ± 0.01	7.1 ± 0.3
butyrolactone	0.21 ± 0.01	3.2 ± 0.1
tetrahydrofuran	0.31 ± 0.01	8.78 ± 0.09
ethylmethylketone	0.30 ± 0.01	6.1 ± 0.2
acetone	0.26 ± 0.01	5.03 ± 0.05
ethanol	0.29 ± 0.01	4.20 ± 0.04
acetonitrile	0.20 ± 0.01	2.9 ± 0.1
chloroform	0.45 ± 0.01	12.3 ± 0.5
chlorobenzene	0.32 ± 0.01	8.01 ± 0.08
1,1,1-trichloroethane	0.32 ± 0.01	7.7 ± 0.2
diethylene glycol diethyl ether	0.32 ± 0.01	5.9 ± 0.1
decahydronaphthalene	insoluble	2.3 ± 0.1
cyclohexane	insoluble	2.60 ± 0.02

Table 2. Poly(ethylene oxide)

* all values ± 0.01

solvent	temperature (°C)	intrinsic * viscosity (dl/g)	swelling
nitrobenzene	20	* 0.33	10.4 ± 0.1
nitrobenzene	60	0.40	10.4 ± 0.1
dimethyl phthalate	60	0.30	9.4 ± 0.2
1,1,1-trichloroethane	30	0.25	8.3 ± 0.4
toluene	60	0.21	5.8 ± 0.2
1,2-dichloroethane	20	0.37	12.1 ± 0.4
acetonitrile	20	0.25	8.1 ± 0.3
methyl benzoate	30	0.35	11.5 ± 0.7
chlorobenzene	20	0.33	9.7 ± 0.4
acetone	30	0.22	5.5 ± 0.1
chloroform	20	0.38	15.6 ± 0.2
butyrolactone	20	0.36	10.1 ± 0.4
dioxane	20	0.35	9.1 ± 0.3
benzene	20	0.32	9.3 ± 0.5
triacetin	60	0.26	5.8 ± 0.1
ethylmethylketone	40	0.17	5.3 ± 0.2
methanol	20	0.30	7.4 ± 0.2
tetrahydrofuran	40	0.21	7.4 ± 0.4
ethanol	40	0.21	4.3 ± 0.2
methylisobutylketone	50	0.16	3.4 ± 0.3
methyl salicylate	20	0.33	9.4 ± 0.2
dichloromethane	20	0.31	13.7 ± 0.3
diethylene glycol diethyl ether	50	0.19	3.6 ± 0.1
water	3	0.49	10.6 ± 0.2
water	10	0.41	9.9 ± 0.2
water	20	0.39	9.0 ± 0.2
water	40	0.33	7.5 ± 0.2
water	60	0.31	6.1 ± 0.2
water	80	0.27	4.9 ± 0.2

In every case, we find a correlation between the swelling at equilibrium of the network and the intrinsic viscosity of its precursor polymer, in the way expected by the theory (Fig. 1). In some cases, there may be a linear relationship. Diethyleneglycol diethylether at 50° and 3,3-dimethyl-2-butanone are given as θ -solvents for PEO. It is indeed under these conditions that the minimal swelling and intrinsic viscosity occur, as would be expected. We have no data on θ-solvents for PPO but we can observe that those solvents giving swellings of 2.6 or less for our network give turbid solutions with the linear polymer and so are bad solvents. The intersection of the regression line of Figure 1a with the line with an ordinate of 2.6 consequently probably give us the co-ordinates of a θ -solvent. Under such conditions, acetonitrile at 20° would be a θ-solvent for PPO.

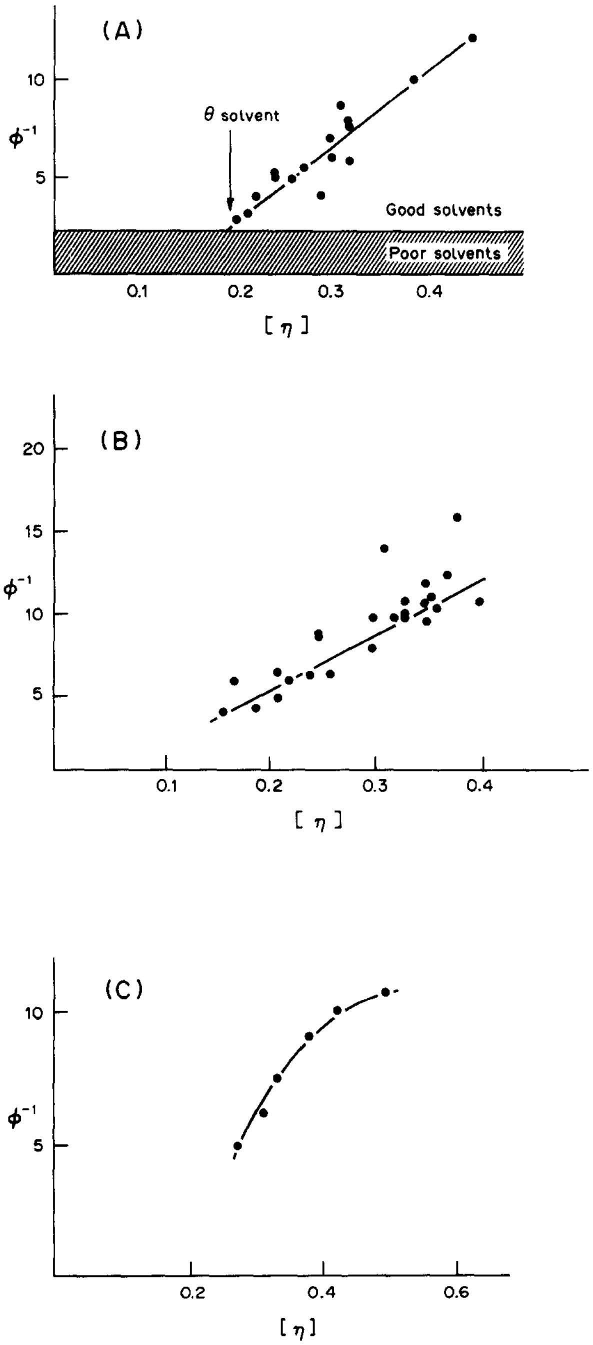

FIGURE 1. Relation between the swelling of a network and the intrinsic viscosity of the linear polymer.
A - PPO-TDI: B - PEO-BTHI:
C - Network PEO-BTHI swollen in water at various temperatures.

For the network PEO swollen in water at various temperatures, we see less dispersion of the results, showing that there is no linear relation between the two parameters (Figure 1c). If, on the other hand, we consider that we have a linear relationship (the correlation coefficients are 0.88 and 0.85), the two figures are not strictly proportional. We can also notice that the swelling varies to a greater extent than the intrinsic viscosity. The reason is that the network has the possibility of stretching chains around crosslinks, whereas the linear polymer cannot (2). The variations in hydrodynamic radius of the linear polymer can only result from some stretching of the chains by some interaction of excluded volume. The phenomenon at the origin of these variations is thus purely local. In the case of a network, in addition to that phenomenon, there are notable possibilities of local reorganization allowing elementary chains to unravel themselves without modifying their conformation. It has been shown (2) that swelling of the network is possible without modifying the radius of gyration of the chains between crosslinks.

CONCLUSION

There is a correlation between the swelling of a network and the intrinsic viscosity of its precursor polymer but there is no strict proportionality. For a given network, the swelling varies to a greater extent than the viscosity of the linear polymer.

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