Thermal Effects of Interaction between Macronet Isoporous Styrene Polymers and Solvents or Precipitators for Linear Polystyrene

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Synopsis

A study has been made of the heats of swelling of macronet isoporous polymers of styrene in toluene and methanol. The swelling of hypercrosslinked networks (degree of crosslinking $\geqslant 40\%$) is shown to be accompanied by liberation of large amounts of heat: 30 and 25 cal/g, respectively. The small difference in the heats of swelling in these media is indicative of small differences in the energy of dispersional interactions of exposed polystyrene chains with "good" and "poor" solvents. This conclusion is corroborated by calculations of the free energy of interaction between hypercrosslinked networks and organic solvents from the isotherms of sorption of their vapors. ΔG reaches high values (500–600 cal/mol) independently of the solvent nature.

INTRODUCTION

In a previous review[1] we showed that a dense crosslinking of polystyrene chains in the presence of large amounts of a thermodynamically good solvent leads to formation of gels with molecularly disperse loose networks. On removing the solvent from the gel, the polymer network shrinks and gets into a highly stressed (compressed) state. The tendency for relaxation of the stresses involved is responsible for the capacity of highly crosslinked macronet isoporous polymers to swell in practically any liquid media.[2,3]

This paper summarizes the results of a calorimetric study into the integral heats of interaction of polymers with toluene, which is a good solvent for linear polystyrene and with methanol which makes polystyrene to precipitate from its solutions.

EXPERIMENTAL

The macronet isoporous polymers (terminology is explained in Ref. 4) were obtained by crosslinking linear atactic polystyrene of $\overline{M}_w = 300,000$, dissolved in dichloroethane (type I) or a copolymer of styrene with divinylbenzene (DVB) swollen to the maximum in the same solvent (type II) by means of monochloro-dimethyl ether as follows:

Type I: Polystyrene (obtained by radical polymerization) and monochloro-dimethyl ether (0.1–0.5 mol/mol monostyrene) were dissolved in dry dichloro-ethane. The solution was carefully stirred, 0.1–0.5 mol of stannic chloride was introduced, and the mixture was quickly agitated once more. (When 0.3–0.5 mol of crossagent reacted with polystyrene, the solution was cooled to $-15°C$ before the catalyst was added). In all experiments 1 g of polystyrene was dis-

solved in 8 mL of the mixture of solvent, crossagent, and catalyst. The transparent colored solution was heated at 80°C for 10 h. The resultant swollen gel was crushed and the catalyst was washed off by acetone, 0.5N HCl, and water.

Type II: 5 g of dry beads of styrene, 0.7% DVB copolymer, were swollen in 39 mL of dichloroethane containing 1.82 mL of monochlorodimethyl ether. In 2 h 0.28 mL of stannic chloride in 3 mL of solvent were dropped, and the mixture was agitated at room temperature for 15 h. After this, 2.53 mL of $SnCl_4$ were introduced and the reaction mixture was heated at 80°C for 10 h. Then the beads were filtered, and the catalyst was washed off as above.

Such a crosslinking technique allows the monochlorodimethyl ether to react quantitatively, giving rise to methylene bridges between the phenyl radicals of adjacent polystyrene chains. Therefore, the degree of crosslinking of macronet isoporous polymers was calculated from composition of the initial reaction mixture as a ratio of the crossbridges number to its sum with the number of unsubstituted phenyl rings.[1]

Also examined were styrene–divinylbenzene copolymers of a standard gel structure (type IV) and a macroporous copolymer formed in the presence of n-octane (type III). All polymers were dried in vacuum at 60–80°C until their weight stopped changing.

A glass ampoul with a weighted amount (0.01–0.05 g) of the dry polymer was broken in the cell of a home-made microcalorimeter, containing 2 mL of toluene or methanol. The developing thermal effect was registrated with the aid of a recording potentiometer. The instrument was previously calibrated coulonometrically as well as with reference to the heat of dissolution of KCl in water, equal to 4444 cal/g. The measurements were reproducible to within ±5%.

The results of all measurements are listed in Table I which also gives the swelling capacity of all examined polymers (measured by the centrifuge method) and the total pore volume W_0 (calculated from true and apparent densities of the polymers).

RESULTS AND DISCUSSION

The calorimetrically measured integral thermal effect of the interaction between a crosslinked polymer and the solvent comprises not only the heat of

TABLE I
Heats of Interaction with Solvents and Swelling and Porosity

Polystyrene network type	Degree of crosslinking (%)	Thermal effect (cal/g)		Swelling (mL/g)		W_0 (cm^3/g)
		Toluene	Methanol	Toluene	Methanol	
I	5	8.0	0	6.29	0.04	0
I	11	8.6	0.8	3.43	0.06	0
I	25	18.0	6.5	3.25	0.25	0.21
I	43	24.0	15.9	3.71	3.08	0.36
I	66	28.6	24.2	4.15	4.10	0.44
I	100	30.3	24.9	3.81	3.84	0.51
II	100	31.4	23.0	0.96	1.02	0.32
III	30	10.4	4.4	1.44	1.16	1.15
IV	2	6.1	0	2.23	0.05	0
IV	20	9.4	0	0.46	0.08	0

swelling of the network but also the thermal effects of wetting, which are particularly manifest in the porous samples. In any event, however, what we measure is the difference between the energy of dispersional polymer–solvent interactions (E_{ps}) and the energies of intermolecular interactions within the solvent phase (E_{ss}) and polymer phase (E_{pp}) separately:

$$E = E_{ps} - E_{ss} - E_{pp}$$

Comparison of different polystyrene samples tells us how the internal structure of the network affects the energy of chain interactions (E_{pp}). By changing the solvent species, we can compare energies of solvation of polystyrene with toluene and methanol (E_{ps}).

In all the systems examined, the interaction between the polymers and solvents is an exothermic process.

The copolymers of styrene with divinylbenzene having a gel structure (type IV) have been produced in the absence of any solvent, that is, under conditions where the contacts between polystyrene chains are the closest. The swelling of the slightly crosslinked polymers in toluene is accompanied by a small thermal effect (6 cal/g) of the same order of magnitude as the dissolution of linear polystyrene in good solvents.[5,6] The increasing content of divinylbenzene in the gel-type copolymer loosens the network structure somewhat because each divinylbenzene crosslink makes two polystyrene chains intersect at a right angle,[7] which eventually results in the more pronounced thermal effect of swelling (despite the decreasing swelling ratio).

In the macroporous styrene copolymers (type III) the interaction between polymer chains is still weaker because of the high content of DVB and high porosity of the polymers. The heat of swelling of the macroporous structures in toluene already becomes as high as 10.4 cal/g.

In the macronet isoporous polymers I and II, the interaction between the polystyrene chains is weakened considerably, which is due to network formation in the presence of large amounts of the thermodynamically active solvent and rigid bridges hindering the approach of one polymer chain to another. Only at a small amount of crosslinks ($\leqslant 10\%$) these polymers exhibit properties similar to those of standard gel copolymers. However, in hypercrosslinked polymers (with the degree of crosslinking exceeding 40%), the energy of interchain interactions (E_{pp}) is weakened by 20–25 cal/g. To put it the other way around, this amount of energy accumulated within the hypercrosslinked network in the form of internal stresses and is released on expansion of the network. Anyway, the solvation of hypercrosslinked polystyrene with toluene is accompanied by the liberation of an extremely large amount of heat: 28–30 cal/g.

Interestingly, the heat of interaction of hypercrosslinked polymers with methanol (precipitator for polystyrene) is also extremely high: ˙25 cal/g. The only explanation is that a significant amount of polystyrene chains in the loose networks of polymers I and II is accessible to methanol. On the contrary, gel and macroporous structures IV and III can interact with methanol only through their surface layers with the result that the thermal effect is either nil or very insignificant (4 cal/g). The latter figure agrees well with the values of heats of sorption of organic solvents by macroporous polystyrene sorbents of the Amberlite XAD type.[8]

As can be inferred from the above, there seem to be no appreciable differences in the energy E_{ps} of dispersional interactions of polystyrene with toluene which

TABLE II
Free Energy ΔG of Sorption of Vapors of Organic Solvents at Volume Fractions of Polymer and
Solvent Equal to 0.8 and 0.2, Respectively

Type of polystyrene structures	S^a (m^2/g)	ΔG (cal/mol)					Ref no.
		Benzene	Methanol	Cyclohexane	Hexane	Heptane	
Linear polystyrene	7.6	−138	−14	−24	—	—	9
Porous linear polystyrene[b]	50.6	−200	−80	−50	—	—	10
III (20% DVB)	38.1	−220	−70	−140	—	—	10
I[c]	950	−510	—	−450	—	—	10
II	1740	—	−540	—	−650	−540	

[a] Inner specific surface area.
[b] Produced by reprecipitation from a benzene solution into methanol.
[c] Crosslinked with p-xylylenedichloride; degree of crosslinking = 100%.

is a thermodynamically "good" solvent and methanol which is a thermodynamically "poor" one. Just like toluene, methanol is capable of energetically solvating polystyrene chains. This finding is consistent with the fact that hypercrosslinked polystyrene networks I and II swell in methanol to the same extent as in toluene (Table I).

The above conclusion is corroborated by calculating the values of free energy ΔG of the interaction of different polystyrene types with vapors of organic solvents from the sorption isotherms (Table II). In the case of linear polystyrene and macroporous copolymers of styrene with DVB, ΔG of sorption of methanol and cyclohexane vapours is low (as compared to benzene) and proportional to the polymer surface accessible to vapors. On the contrary, hypercrosslinked polystyrene networks I and II exhibit extremely high energies of interaction both with "poor" (methanol, cyclohexane, hexane, heptane) and "good" (benzene) solvents, reaching as high as 500–600 cal/mol.

CONCLUSION

It is customary to assume that solvents which are unable to dissolve a linear polymer and increase the volume of its crosslinked analog are thermodynamically poor and do not solvate polymer chains. However, our data show the arbitrary nature of such a subdivision of liquids into solvating and nonsolvating ones. The fact of dissolution or swelling of a polymer is only indicative of the type of interaction—polymer–polymer or polymer–solvent—that is preferable in a given system, without telling anything at all about the magnitude of these interactions. In fact, the difference in the energies of interaction of exposed polymer chains with solvating and nonsolvating media is extremely small as compared to the magnitude of the thermal effects of solvation.

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