

Dynamic and Equilibrium Swelling of DVB-Crosslinked Polystyrene Particles

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Synopsis

The dynamic and equilibrium swelling behavior of polystyrene microparticles crosslinked with divinyl benzene was investigated in methyl ethyl ketone and cyclohexane. The dynamic studies gave new information about the mechanism of penetrant transport in this polymer. The equilibrium studies were used to determine important parameters of the crosslinked structure of these systems, including the average molecular weight between crosslinks, \bar{M}_c .

INTRODUCTION

Polystyrene microparticles are important in a variety of applications including their use in chromatography, as ion exchange resins, as packing material in fixed bed reactors, and in controlled release of agricultural products upon sulfonation.

Although numerous publications have presented the reaction procedure and the particle size distribution^{1,2}, only a handful of research contributions have examined the molecular weight between crosslinks, \bar{M}_c , as a function of reaction conditions. Notable exceptions are the contributions of Geschke et al.³ and Barar et al.^{4,5} The general conclusions of these studies are that the molecular weight between crosslinks is affected by the ratio of divinylbenzene to styrene, and, in turn that as \bar{M}_c increases, i.e., the degree of crosslinking decreases, the degree of swelling in various solvents increases.

The dynamic swelling properties of polystyrene microparticles in certain penetrants have been studied by Ensore et al.⁶ This study concluded that *n*-hexane uptake in particles of approximately 200 μm in diameter could be characterized by Case-II transport whereas the solvent uptake in particles of approximately 0.5 μm could be characterized by Fickian diffusion. This observation, although somewhat confusing to uninitiated readers, is typical of transport of penetrants in glassy polymers where relaxation and diffusion mechanisms may or may not be coupled.⁷

Highly crosslinked polystyrene microparticles have been used in this study to analyze their crosslinked structure. These particles were produced via suspension polymerization in an aqueous phase containing a suspending agent.

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EXPERIMENTAL

Preparation of Polystyrene Particles

Styrene was distilled *in vacuo*. The organic phase for the suspension polymerization was prepared by mixing divinyl benzene (DVB) and styrene at the desired crosslinking ratio varying from 0.010 to 0.200 mol DVB/mol styrene. The initiator, benzoyl peroxide, was added in the amount of 1 wt % of styrene used. The organic phase was added in a 2:3 volume ratio to the aqueous phase of a 7 wt % poly(vinyl alcohol) solution in a three-neck flask.

The suspension was heated initially at 65°C for 5 min, and then the temperature was increased to 90°C where it was kept constant for approximately 6 h. The agitation was maintained at a constant rate in the range from 650 to 1000 rpm, depending on the desired particle size. Larger particles required slower agitation; if the agitation was too slow, no suspension was obtained.

After the polymerization was complete, the final dispersion was cooled, filtered, washed with methanol and hot water, and the particles were dried. After drying, the particles were sieved to the desired size ranges using ASTM sieves from 6 to 100 mesh (3350—150 μm).

Swelling Studies

Dynamic swelling studies were carried out in a thermogravimetric analyzer (TGS-2, Perkin Elmer, Norwalk, CT) using methyl ethyl ketone as the penetrant, at a constant temperature of 35°C. The penetrant uptake M_t , per gram of dry polymer M_p , was reported as a function of time. This technique has an experimental error of 0.5%.

For the equilibrium swelling studies, approximately 2–3 g of polystyrene particles were placed in a glass jar and solvent was added to fill the jar. The sealed container was then placed in a water bath to maintain a constant temperature of 35°C. The swelling agent, cyclohexane or methyl ethyl ketone, was changed daily for 5 days. After equilibrium was reached, the solvent was decanted off, and the swollen volume of the particles was determined by displacement of a known volume of heptane. The dry weight was then determined by drying under vacuum until a constant weight was obtained.

RESULTS AND DISCUSSION

Dynamic Swelling Studies

Dynamic swelling studies were carried out using methyl ethyl ketone vapor as the penetrant at 35°C. For polystyrene particles with crosslinking ratios of 0.075 and 0.15, less than 2% penetrant uptake was measured after 48 h; Figure 1 presents these results, with the most crosslinked sample leading to a lower equilibrium uptake value.

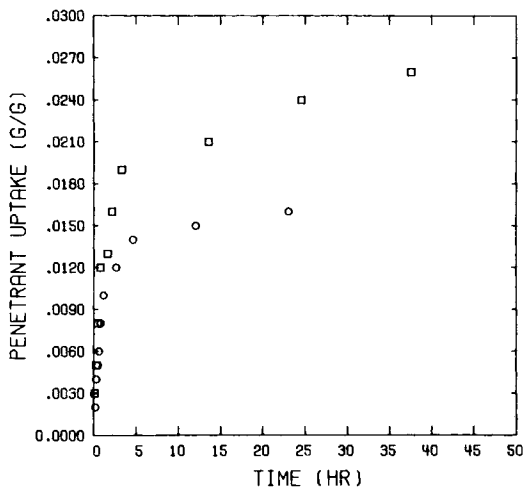


Fig. 1. Methyl ethyl ketone uptake per gram of dry, crosslinked polystyrene as a function of transport time at 35°C. Sample with crosslinking ratio $X = 0.075$ (□); sample with $X = 0.15$ (○).

Dynamic transport of methyl ethyl ketone is characterized by smooth uptake curves. The results may be analyzed with the simple exponential expression of

$$\frac{M_t}{M_p} = kt^n \quad (1)$$

where n is characteristic of the transport mechanism. For the first 60% of the uptake the exponent was calculated as 1.10 for the polystyrene with $X = 0.15$, and 1.13 for the polystyrene particles with $X = 0.075$; both studies were done with microparticles of 425–600 μm size. It is evident that in this range of particle sizes the penetrant transport is still Case-II, despite the wide thermodynamic differences of the two penetrants used, i.e., *n*-hexane in the study of Enscoe et al.⁶ and methyl ethyl ketone in the present work.

The front movement of methyl ethyl ketone at 30°C was measured as a function of time for a polystyrene (with $X = 0.15$) particle with an initial diameter of 380 μm . A photomicrographic picture with the penetrant front at 90 min is shown in Figure 2. The constant velocity of the penetrant front was calculated from these studies as 0.026 $\mu\text{m/s}$ with a correlation coefficient of 0.98.

Equilibrium Swelling Studies

Methyl ethyl ketone and cyclohexane were used as swelling agents at 35°C. The equilibrium swelling studies provided the data from which the volume fraction of polymer at equilibrium, $v_{2,\text{app}}$, was calculated.

To calculate the true equilibrium volume fraction of polymer in the particles, $v_{2,s}$, it is necessary to correct $v_{2,\text{app}}$ for the amount of penetrant which has filled the holes of the porous structure without effectively contributing

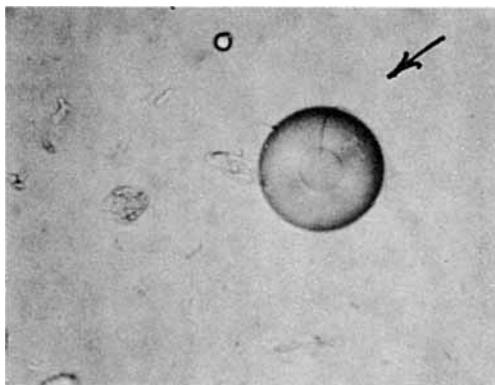


Fig. 2. Dynamic transport of methyl ethyl ketone in a particle of crosslinked polystyrene ($X = 0.15$) with initial diameter of $510 \mu\text{m}$. The photograph shows the distinct front formed between the inner glassy core and the outer rubbery (swollen) layer of the particle.

to polymer swelling. For polystyrene, previous mercury porosimetry studies⁵ have shown that the porosity of the particles was such that it did not affect the analysis of the data, and that the apparent volume fraction of the swollen particles, $v_{2,\text{app}}$, and the true volume fraction of the polystyrene proper, $v_{2,s}$, did not differ more than 1%.

The modified Gaussian network⁸ equation (2) was applied to the results of the equilibrium studies to determine the molecular weight between crosslinks, \overline{M}_c :

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\overline{v}/V_1) [\ln(1 - v_{2,s}) + v_{2,s} + \chi v_{2,s}^2] [1 - 1/Nv_{2,s}^{2/3}]^3}{(v_{2,s}^{1/3} - \frac{1}{2}v_{2,s}) [1 + 1/Nv_{2,s}^{1/3}]^2} \quad (2)$$

where

$$N = \frac{\lambda \overline{M}_c}{M_r} \quad (3)$$

Here, \overline{M}_n is the number average molecular weight of the original polymer chains before crosslinking, $v_{2,s}$ is the polymer volume fraction of the swollen network, χ is the thermodynamic interaction parameter for the polymer/penetrant pair at $v_{2,s}$ and T , \overline{v} is the specific volume of the polymer, V_1 is the molar volume of the swelling agent, M_r is the molecular weight of the repeating unit ($M_r = 104$), and λ is the number of links per repeating unit ($\lambda = 2$).

The value of χ for polystyrene/cyclohexane as a function of concentration is given by Cantow and Schuster.⁹ For polystyrene/methyl ethyl ketone, the χ factor is given by Bawn et al.¹⁰ The value of \overline{M}_n was assumed to be 50,000 for reasons discussed before.¹¹ The results of this analysis are tabulated in Tables I and II for 600–850 μm particles of polystyrene swollen at 35°C in cyclohexane and methyl ethyl ketone, respectively. These results are presented graphically in Figure 3. As the crosslinking ratio X is in-

TABLE I
Molecular Weight between Crosslinks as a Function of Crosslinking Ratio for 600–850 μm Particles of Polystyrene Swollen by Cyclohexane at 35°C

Crosslinking ratio X (mol DVB/mol Styrene)	Molecular weight between crosslinks, \bar{M}_c	Number of repeating units between crosslinks	Mesh size in swollen state, ξ (\AA)
0.010	8,450 \pm 100	81.3	62.8
0.030	7,000 \pm 150	67.3	55.1
0.050	2,900 \pm 150	27.9	33.4
0.075	1,400 \pm 150	13.5	21.1
0.100	1,000 \pm 100	10.4	16.8
0.150	1,100 \pm 140	10.6	18.2
0.175	1,050 \pm 130	10.0	17.6
0.200	1,100 \pm 140	10.6	18.2

TABLE II
Molecular Weight between Crosslinks as a Function of Crosslinking Ratio for 600–850 μm Particles of Polystyrene Swollen by Methyl Ethyl Ketone at 35°C

Crosslinking ratio X (mol DVB/mol Styrene)	Molecular weight between crosslinks, \bar{M}_c	Number of repeating units between crosslinks
0.075	1,800 \pm 130	17.3
0.100	1,800 \pm 120	17.3
0.125	1,000 \pm 150	9.6
0.150	860 \pm 75	8.3
0.175	1,050 \pm 150	10.0
0.200	680 \pm 50	6.5

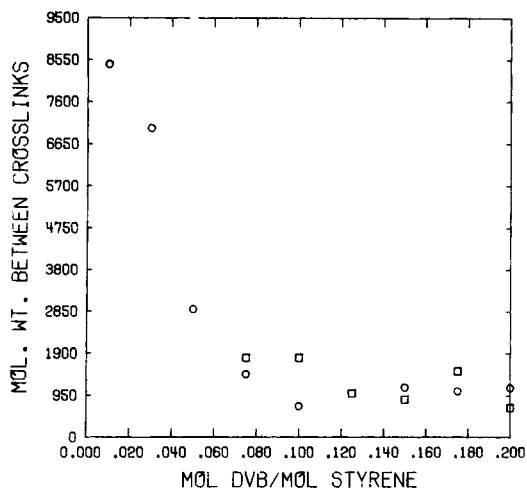


Fig. 3. Molecular weight between crosslinks, \bar{M}_c , as a function of crosslinking ratio X for polystyrene microparticles of 600–850 μm . Results are presented as calculated from equilibrium swelling in cyclohexane at 35°C (○) or in methyl ethyl ketone at 35°C (□).

creased, the molecular weight between crosslinks decreases. Differences between the molecular weight between crosslinks as determined by the cyclohexane and methyl ethyl ketone studies are probably the result of experimental error in the determination of χ .

From the previous analysis one can determine also the effective mesh size of the network as described by the correlation length ξ . For this, the procedure of Flory was used.¹² From the data of Table I the end-to-end distance in the freely jointed state was determined as

$$r_f = l \sqrt{N} \quad (4)$$

where $l = 1.54 \text{ \AA}$ and the number of links, N , is given by eq. (3). Then, the end-to-end distance in the unperturbed state was calculated through the characteristic ratio $C_n = 10$ reported by Flory¹³:

$$\bar{r}_0^2 = C_n \bar{r}_f^2 \quad (5)$$

Finally the end-to-end distance in the swollen state, equivalent to the correlation length ξ , was calculated as

$$\xi = v_{2,s}^{-1/3} r_0 \quad (6)$$

Table I shows the values of the mesh size ξ (\AA). It was further observed that the molecular weight between crosslinks decreases as the particle size increases for the same nominal crosslinking ratio. This phenomenon is the result of the suspension polymerization method, where the particles become progressively more crosslinked from the center to the surface. The phenomenon is shown by the results of Figure 4 for polystyrene particles with a crosslinking ratio of 0.03.

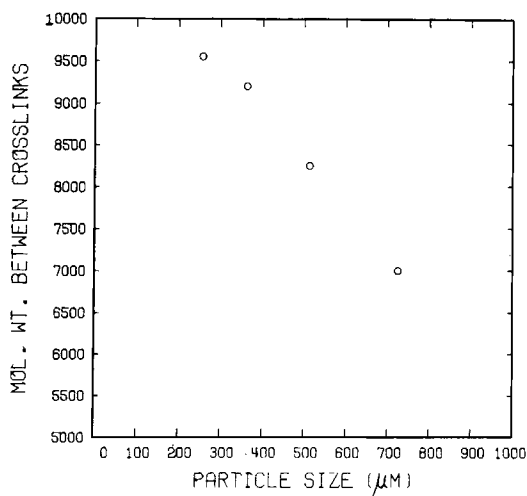


Fig. 4. Molecular weight between crosslinks, \bar{M}_c , as a function of particle size in (μm) for polystyrene microparticles of $X = 0.03$. Results are from equilibrium swelling studies in methyl ethyl ketone at 35°C .

CONCLUSIONS

Equilibrium swelling studies can be used to determine the average molecular weight between crosslinks, \overline{M}_c , of crosslinked microparticles and thus study either the progress of a crosslinking reaction or the size of the diffusional space between macromolecular chains.

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