

THE MECHANISM OF COPOLYMERIZATION OF VINYL AND DIVINYL MONOMER VI: A STUDY ON THE MECHANISM OF THE STRUCTURE FORMATION OF CROSSLINKED POLYSTYRENE

WANG Shouting(王寿亭), CHEN Weizhu(陈伟朱), JIANG Lu(姜 鹭) and HE Binglin(何炳林)
(Institute of Macromolecular, Nankai University, Tianjin)

ABSTRACT

In order to study the mechanism of the formation of macroporous copolymer, the overall reaction kinetics, phase separation and gelation of the S/EGDM in the presence of inert solvents and the physical properties of the copolymer were investigated and compared with the corresponding system of S/DVB and S/DVB/MMA. The formation of the network structure of the macroreticular polymer was studied and a model of the mechanism suggested.

The matrix of macroporous crosslinked polystyrene has been used widely. In order to meet the needs of different fields, we have synthesized matrixes of different structures by changing the concentration and property of the cross-linking agent and inert solvents. The mechanism of the formation of the macroreticular structure has been studied^[1-3] and in accordance with experiments, we continue to investigate the overall kinetics and phase separation of the copolymerization of styrene/ethylene glycol α , α' -dimethylacrylate (S/EGDM) in the presence of inert solvents. We also investigate the physical properties of the corresponding copolymers, from which we try to understand the mechanism of the formation of the macroporous products.

EXPERIMENTAL

Chemicals

Styrene, in which the inhibitor was removed with 201 strong anion exchanger, was distilled at 55–56°C/17mmHg under nitrogen atmosphere. Refractive index $n_{20^\circ\text{C}} = 1.5460$.

EGDM was synthesized according to reference[4]. The product was distilled under vacuum and analysed with gas chromatography. The product contains 98% EGDM, $n_{20^\circ\text{C}} = 1.4540$.

DVB, commercial reagent, in which the inhibitor was removed with strong anion exchanger, was analysed with gas chromatography. It contains 17.29% p-DVB, 28.18% m-DVB, 14.14% p-EVB, 32.20% m-EVB and the rest diethylbenzene. Other chemicals are all A.R..

Kinetics

The solution of vinyl and divinyl monomer mixtures containing 1% Bz_2O_2 and 100% inert solvents were mixed with stirring, then placed into thirteen vials which were then chilled with liquid nitrogen, evacuated and purged with dry nitrogen three times before sealed. The sealed samples were placed in the reaction system at 40°C and then raised to 80°C at a rate of 2°C/min. as the starting reaction point. The monomers remained in the system were analysed with chromatography at intervals. The rate of transformation was calculated. The analysis of S/EGDM

was carried out with Backman 443 HPLC, whereas for S/DVB with Type100 gas chromatography.

Phase Separation and Gelation

The measurements of phase separation and gelation during the copolymerization were described in reference[3].

RESULTS AND DISCUSSION

The effect of cross-linking agent and porogenic agent on kinetics

The total conversion of the S/EGDM and S/DVB at different amount of cross-linking agent is shown in Fig.1. The corresponding conversion of individual monomer is indicated in Fig.2.

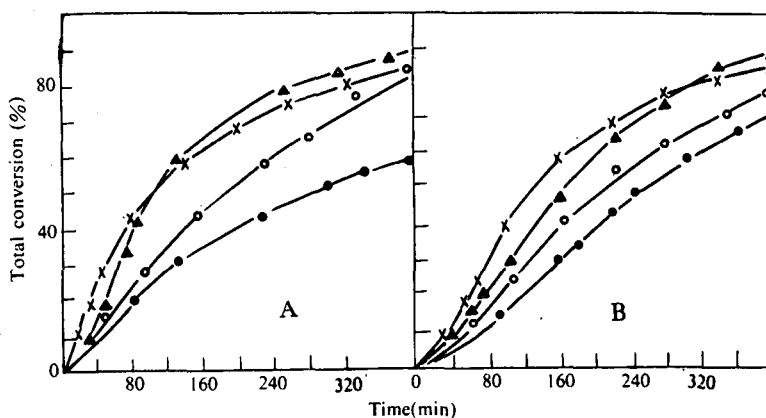


Fig.1 Total conversion of S/EGDM(A) and S/DVB(B) with *n*-heptane as the porogenic agent
Concentration of cross-linking agent (mol%): ● 3.24; ○ 5.56; ▲ 9.10; × 11.6.

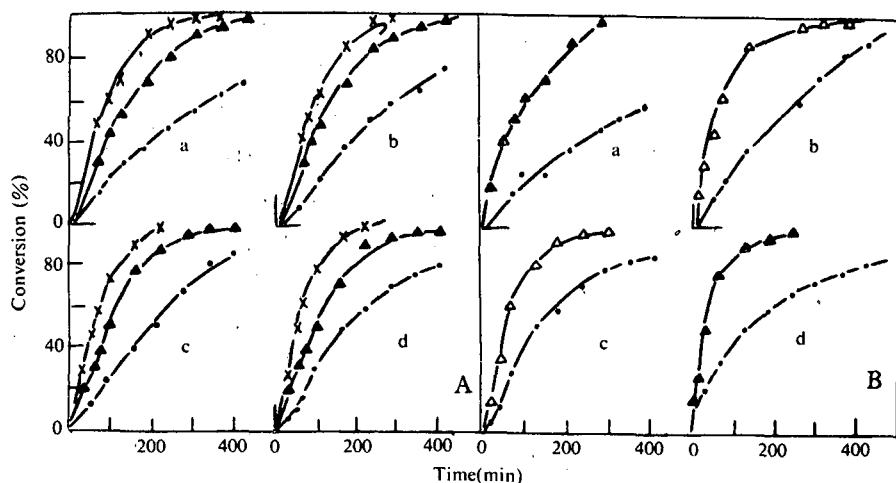


Fig.2 Conversion of individual monomer of S/DVB(A) and S/EGDM(B) in the presence of *n*-heptane
A: ● styrene, ▲ *m*-DVB, × *p*-DVB. B: ● styrene ▲ EGDM.
Conc. of crosslinker (mol%): a, 3.14; b, 5.56; c, 9.10; d, 11.6.

Fig.1 indicates that the rate of copolymerization increased as the amount of crosslinker was

increased. The conversion of the monomer crosslinked by EGDM was higher than that cross-linked by DVB when the copolymerization was in the initial stage. On the contrary, when the conversion was high, the rate of copolymerization was in the opposite order. In both copolymerization systems, the conversion of the divinyl compound was higher than that of the vinyl monomer at a definite time. This would cause the distribution of the crosslinker in the polymer network heterogeneous unless the reactivity ratios of the crosslinker and styrene are both equal to one. The heterogeneity in the polymer network crosslinked by EGDM is even more serious than that by DVB.

The effect of porogenic agents on the rate of copolymerization is shown in Fig.3.

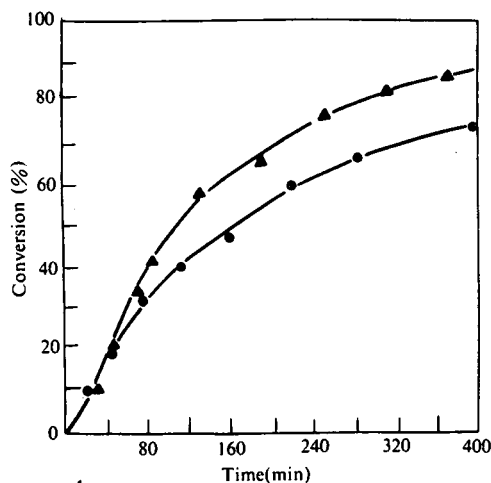


Fig.3 Conversion of S/EGDM in the presence of different porogenic agents

● n-butyl ether; ▲ n-heptane.

As a solvent, the n-butyl ether ($\delta = 7.8$) is better than that of n-heptane ($\delta = 7.4$) for polystyrene ($\delta = 9.1$). Fig.3 indicates that the poorer is the solvent as a porogenic agent, the faster the rate of copolymerization. This is due to the fact that the chain radical in a non-solvent becomes so shrinkable and insoluble that the termination is more difficult. Besides, as the chain radical precipitated out, the concentration of monomer around it might become higher.

The effect of cross-linking agent and porogenic agent on gelation

From Table 1, it is evident that the higher is the concentration of the cross-linking agent, the shorter the time required for gelation when the other conditions are the same. However, the time of gelation is not a linear function of the amount of cross-linking agent used for the copolymerization. The change of gelation time becomes slower and slower as the amount of cross-linking agent increases.

Table 1 also indicates that at lower concentration of cross-linking agent the time of gelation for styrene cross-linked by EGDM is shorter than that cross-linked by DVB and the total conversion of S/EGDM at gelation point is lower. This accounts for the fact that pendent vinyl group of EGDM in the chain radical possesses higher activity.

The effect of crosslinking agent and porogenic agent on phase separation

During polymerization, the phase separation arises from the syneresis of the network.

Table 1 The relation between the gelation point and polymeric system

Inert solvents	S/EGDM system					S/DVB system				
	Conc. of cross-linker(mol%)	Monomer	Conversion at G.P. (%)	Molar por-tion at G.P. in network	Time to G.P. (min.)	Monomer	Conversion at G.P. (%)	Molar por-tion at G.P. in network	Time to G.P. (min.)	
n-heptane	3.24	EGDM	40.0	0.077	57	DVB	41.1	0.045	80	
		S	16.0	0.923		S	29.0	0.955		
	5.56	EGDM	24.0	0.150	32	DVB	50.0	0.111	65	
		S	8.0	0.850		S	23.5	0.889		
	9.10	EGDM	9.0	0.311	11	DVB	32.5	0.207	57	
		S	2.0	0.689		S	12.5	0.793		
	11.6	EGDM	3.0	0.079	5	DVB	25.2	0.248	56	
		S	4.6	0.921		S	10.0	0.752		
	3.24	EGDM	48.0	0.063	71	DVB	46.8	0.050	75	
		S	24.0	0.937		S	30.0	0.950		
n-butyl ether	5.56	EGDM	35.0	0.105	35	DVB	37.4	0.104	61	
		S	17.5	0.895		S	19.0	0.896		
	9.10	EGDM	22.0	0.180	24	DVB	36.8	0.221	50	
		S	10.0	0.820		S	13.0	0.779		
	11.6	EGDM	25.0	0.179	19	DVB	25.5	0.358	51	
		S	15.0	0.821		S	6.0	0.642		

Increasing the amount of crosslinking agent, the phase separation of the system is evident (Fig.4). When the solvating ability of porogenic agent decreases from *n*-butyl ether to *n*-heptane, the phase separation becomes more and more evident (Fig.5).

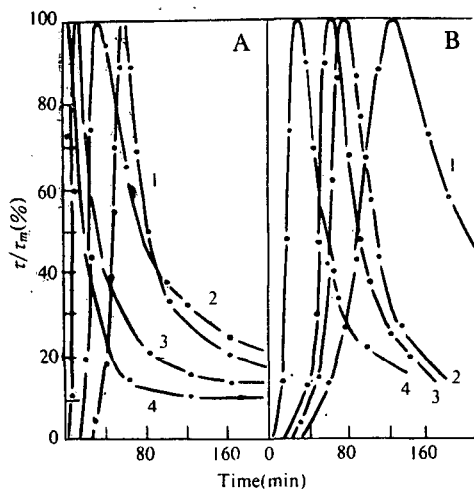


Fig.4 Phase separation of different systems in the presence of *n*-heptane.

A S/EGDM, B S/DVB.

Conc. of crosslinker (mol%):

1 3.24, 2 5.56, 3 9.10, 4 11.6

τ turbidity, τ_m maximum turbidity

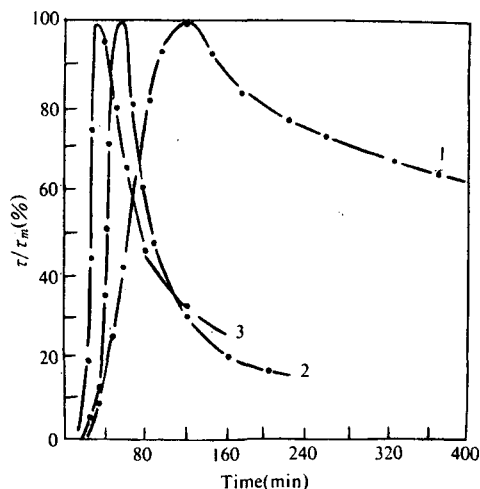


Fig.5 Phase separation of S/EGCM in the presence of different porogenic agents

1 *n*-butyl ether; 2 200# gasoline; 3 *n*-heptane.

τ turbidity, τ_m maximum turbidity

Physical properties of copolymer

Polystyrene and chloromethylated polystyrene crosslinked by EGDM have higher swelling capacity. The swelling capacity of S/DVB/MMA, which has equal amount of ester groups and

Table 2 Swelling parameters, $(v_0 - v)/v_0$, of copolymers and CME-beads

Sample	Solvent	Conc. of crosslinker(mol%)		
		3.24	5.56	9.10
S/EGDM copol.	Toluene	5.35	2.90	1.70
	Acetone	1.00	0.90	0.75
S/DVB copol.	Toluene	2.35	1.80	0.95
	Acetone	0.80	0.75	0.55
S/DVB/MMA copol.	Toluene	2.50	1.75	0.83
	Acetone	1.00	0.78	0.53
S/EGDM CME-beads	Toluene	3.10	2.40	1.90
	Acetone	1.90	1.75	1.60
S/DVB CME-beads	Toluene	1.30	1.30	0.90
	Acetone	1.00	1.00	0.70

percentage of crosslinking agent with S/EGDM, is approximately equal to that of S/DVB (Table 2).

In polarizing point of view, it is understood that S/EGDM in acetone has greater swelling capacity than that of S/DVB. Why does it possess the greater swelling capacity in toluene? This may be explained as follows: In both the polystyrene either crosslinked by EGDM or by DVB, the distribution of EGDM in S/EGDM is more heterogeneous. The polystyrene with low crosslinking in S/EGDM has greater swelling capacity.

Compare the behaviour of the kinetics and phase separation of S/DVB/MMA with that of S/EGDM and S/DVB (Fig.6,7), it can be seen that that of S/DVB/MMA is similar to that of S/DVB. Therefore, the structure of S/DVB/MMA is similar to that of S/DVB. The swelling capacity of S/DVB/MMA is approximately equal to that of S/DVB.

The porosities of copolymers are shown in Table 3.

The poorer is the inert solvents and the higher is the percentage of the crosslinking agent, the greater the porosity of copolymer within a certain range. Summing up from the role of the phase separation and porosity of copolymers, we can see that the easier the former takes place, the greater is the porosity of the copolymer obtained.

A model of the structure of the formation of macropores

According to the results obtained above and from other author's publication [5], the model of

Table 3 Structure properties of copolymers

Copolymer	Conc. of crosslinker (mol%)	Inert solvent	Apparent density (g/ml)	Skeletal density (g/ml)	Porous volume (g/ml)	Porosity (%)
S/DVB	3.24	200 [#] gasoline	1.0356	1.0483	0.0118	1.22
	5.56		0.7873	1.0601	0.3268	25.73
	9.10		0.6555	1.0661	0.5876	38.52
S/EGDM	3.24		1.0036	1.0443	0.0389	3.90
	5.56		0.9329	0.9990	0.0718	6.70
	9.10		0.7233	1.1193	0.4891	35.38
S/DVB/ MMA	3.24		1.0008	1.0074	0.0065	0.65
	5.56		0.8209	1.0983	0.3076	25.25
	9.10		0.5612	1.1084	0.8798	49.37
S/DVB	3.24	n-butyl ether	1.0162	1.0164	0.0002	0.02
	5.56		1.0195	1.0392	0.0186	1.90
	9.10		0.9746	1.0363	0.0617	5.95
S/EGDM	3.24		1.0197	1.0599	0.0372	3.51
	5.56		1.0511	1.0683	0.0153	1.61
	9.10		1.0008	1.1120	0.0999	9.99

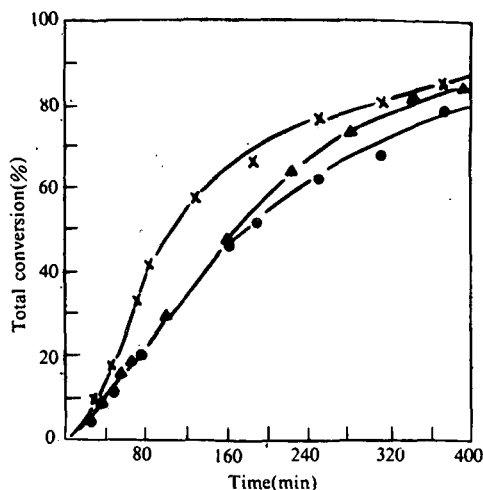


Fig.6 Total conversion of monomers for different systems in the presence of n-heptane

Conc. of crosslinker (mol%), 9.10. System

● S/DVB/MMA; ▲ S/DVB; × S/EGDM.

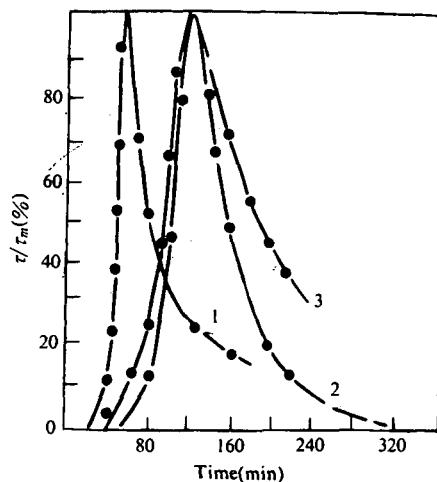


Fig.7 Phase separation of different systems in the presence of n-heptane

Conc. of crosslinker (mol%), 3.24.

System 1 S/EGDM, 2 S/DVB/MMA, 3 S/DVB.

τ , turbidity, τ_m , maximum turbidity.

the structure of the formation of macropore in the presence of inert solvents may be assumed as in Fig.8.

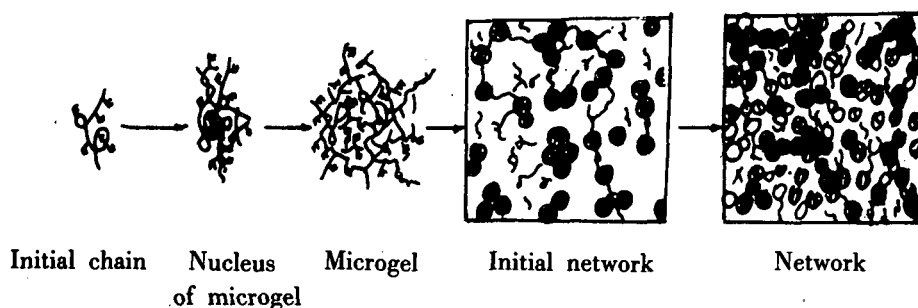


Fig.8 Scheme of the formation of macropores

After initiation by a radical, an initial polymer chain with pendent vinyl groups was formed. The intramolecular [6] or intermolecular crosslinking in the initial stage may produce nucleus of microgel. When microgel nucleus grew large enough, the interfacial tension on the microgel nucleus led to the low-energy spherical form, i.e. a microgel. Then, the radicals on a microgel surface reacted with the pendent vinyl groups on another microgel surface. The initial crosslinked network was thus obtained. Finally, the monomers remained between solution and microgels reacted to form new microgels which were distributed among the initial microgels. A crosslinked network composed of microgels containing relaxed microgels, microgel nucleus and linear polymer was produced.

Keywords:

Kinetics; phase separation; S/EGDM; Copolymerization

REFERENCES

- [1] 陈伟朱, R. 库宁, J. H. 坎累特, “功能高分子学术论文报告会预印集”, 中国, 昆明, 1981, P80.
- [2] Chen weizhu; Zhao Wenzhi; Lin Xue; Song Zhenji and He Binglin, 29th IUPAC International Symposium on Macromolecules, Bucharest, 1983.
- [3] 李效东, 陈伟朱, 刘为焱, 何炳林, 高分子通讯 (*Polymer Communications*), 1986(2), 144.
- [4] Hubca, GH, *Revue Roumaine de Chimie*, 1981, 26, 1185.
- [5] Lun, K. A. and Kunin, R., *J. Polymer Sci., A* 1968, 6, 2689.
- [6] Kast, H. and Funke, W., *Macromol. Chem.*, 1979, 180, 1335.