Vinyl-Divinyl Copolymerization: Copolymerization and Network Formation from Styrene and p- and m-Divinylbenzene

J. Maunsky[a]; J. Klaban[a]; K. Dušek[b]

[a] Research Institute for Synthetic Resins and Lacquers Pardubice, Czechoslovakia [b] Institute of Macromolecular Chemistry Czechoslovak Acadamy of Sciences, Prague, Czechoslovakia

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J. MALINSKÝ and J. KLABAN

Research Institute for Synthetic Resins and Lacquers
Pardubice, Czechoslovakia

and

K. DUŠEK

Institute of Macromolecular Chemistry
Czechoslovak Acadamy of Sciences
Prague 6, Czechoslovakia

SUMMARY

The composition of copolymers of p- and m-divinylbenzene with styrene was determined by infrared spectrometry during copolymerization and compared with values calculated on the assumption that the polymerizing system is homogeneous, and the reactivities both of the vinyl groups in the monomers and of the pendant vinyl groups are independent of the extent of copolymerization. At lower conversions the content of all divinylbenzene units, and especially that of the pendant vinyl groups in the copolymer, is lower than calculated, whereas at higher conversions a fraction of pendant vinyl groups does not react. The conversions at the gel point do not depend on the concentration of divinylbenzene; at higher percentages of the divinyl monomer or dilution of the system they are higher for p- than for m-divinylbenzene, although p-divinylbenzene copolymers contain more divinylbenzene units at the same conversion. The deviations are explained by inhomogeneous copolymerization caused by locally different concentration of the vinyl

groups. At low conversions the concentration of pendant vinyl groups within the domain of the growing macroradical is higher than their average concentration so that the polymerization may proceed locally almost to completion.

INTRODUCTION

Cross-linked copolymers of styrene and divinylbenzene are widely used for the preparation of ion-exchange resins or in the gel permeation chromatography. It has been established that the reactivities of vinyl groups in m- and p-divinylbenzene differ when copolymerized with styrene [1, 2], and that the properties of the final copolymers are also different [3-6]. An investigation of the copolymerization and network formation over the whole range of polymerization conversions can give an answer whether the vinyl groups participating in the copolymerization will effectively preserve their reactivities determined at low conversions and characterized by the published copolymerization parameters. Storey [7] has observed certain anomalies in the dependences of the gel point on concentration of the divinyl monomer, which seem to suggest that at higher concentrations of the cross-linking agent the copolymerizing system is not quite homogeneous and the tendency toward microgel formation can shift the gel point toward higher polymerization conversion. Inhomogeneity of the copolymerizing system, however, would arise as a consequence of the local differences in the concentration of the reacting vinyl groups and would cause an apparent change in their reactivities.

We have, therefore, investigated the dependences of the copolymer composition (content of the divinyl units in the copolymer which reacted either by one or by both vinyl groups) on conversion at various initial compositions and compared the experimental results with the theoretical dependences calculated on the assumption of the independence of the copolymerization parameters on conversion. Conclusions on the cross-linking copolymerization were also supplemented by measurements of the conversion at the gel point and of the increase of the effective cross-linking degree of gels during copolymerization.

EXPERIMENTAL

Preparation of Isomers of Divinylbenzene

m-Divinylbenzene was prepared by preparative gas chromatography from

51.2% technical divinylbenzene (Dow Chemical Co.) having the following composition (determined by gas chromatography): 3.17% m-diethylbenzene, 1.37% p-diethylbenzene, 30.04% m-ethylvinylbenzene, 13.09% p-ethylvinylbenzene, 35.02% m-divinylbenzene, 16.18% p-divinylbenzene, and 1.12% naphthalene. The column, 30 mm bore and 4.2 m long, was filled with Porovina, size 0.20-0.45 mm (Lachema, Brno), impregnated with 10% of ethylene glycol phthalate. Separation was carried out at a column temperature of 145°C, evaporator temperature of 250°C, and nitrogen flow of 500 ml/min. Flame-ionization detection was used. The fractions were purified twice by gas chromatography. p-Divinylbenzene was prepared from technical divinylbenzene by bromination with bromine, separation and purification of p-bis(1.2-dibromoethyl)benzene, and its debromination with zinc according to a procedure described by Storey [7]. The product was repurified by distillation at 1 mm Hg in nitrogen. Styrene (Kaučuk, Kralupy) was freed from inhibitor by extraction with 5% sodium hydroxide and then redistilled under a pressure of 2-3 mm Hg in nitrogen. Dibenzoyl peroxide was recrystallized from chloroform solution.

Investigation of the Course of Copolymerization

Copolymerization of styrene with divinylbenzene was carried out in nitrogen in sealed ampoules, usually at 70°C and concentration of dibenzoyl peroxide 0.3%. At certain time intervals the ampoule were removed from the thermostat, cooled quickly to 0°C, and their contents were transferred into an excess of benzene or toluene. If the polymerization was stopped before the gel point, the polymer was precipitated with methanol from benzene solution, and the product was reprecipitated several times and dried at room temperature in vacuo for 48 hr. In the measurements of the gel point conversion, methanol contained 0.05% of hydroquinone. If the polymerization was stopped after the gel point, the gel was extracted several times at room temperature with an excess of toluene. With the exception of samples analyzed by infrared spectrometry, toluene was stabilized with 0.05% of p-quinone. After extraction and blotting with filtration paper, the weight of the swollen gel was determined; the weight of the dry gel was determined on drying to constant weight at 105°C. Soluble fractions in the extract were precipitated with methanol. The weight polymerization conversion (α_w) was calculated from the weight of the dry polymer; the weight swelling degree, W, is given by the ratio of weights of swollen and dry gels. For gel point determination the ampoule with monomers was fixed in a rotating holder with a thermostat jacket and the motion of the bubble in the

ampoule was observed. The gel point conversion was also determined by extraploating the weight of the gel fraction to zero. The relative error of determination was ±1.5%.

Analysis of the Copolymer Composition

The copolymer composition was determined by infrared spectrometry; the procedure has been partly outlined earlier [2, 8]. The spectra were recorded with a Unicam SP 100 spectrometer, and calibration was made using polystyrene and indene mixtures. The extracted samples were treated using the KBr techniques. They were ground in an electromagnetic vibrator at the temperature of liquid nitrogen for 30 min. The pressed KBr pellets were dried prior to measurement at 1 mm Hg over P_2O_5. Drying is important with respect to the absorption by water in the region 1630 cm^{-1}.

The following bands were used as analytical bands for the determination of the copolymer composition: 1630 cm^{-1} (C:C valency vibration of the vinyl group), 838 cm^{-1} (out-of-plane deformation vibrations of the p-substituted aromatic ring of poly-p—divinylbenzene), 765 cm^{-1} (out-of-plane deformation vibrations of the m-disubstituted aromatic ring of poly-m-divinylbenzene), and 760 cm^{-1} (out-of-plane deformation vibrations of the monosubstituted aromatic ring in polystyrene). The concentration of the divinylbenzene and styrene units in the copolymer was determined from the absorbances ratio A_{795}/A_{760} (copolymers of m-divinylbenzene) and A_{838}/A_{760} (copolymers of p-divinylbenzene). Calibration of these ratios was performed by using mixtures of polystyrene and polydivinylbenzene with pendant vinyls. It has been found, however, that the intensity of the 795 and 838 cm^{-1} bands depends on the content of the pendant vinyls; the absorbances ratio was therefore corrected according to the relationships

$$(A_{838}/A_{760})_{cor} = (A_{838}/A_{760})/[1 + 0.00696(c_{PV})_p] \tag{1}$$

$$(A_{795}/A_{760})_{cor} = (A_{795}/A_{760})/[1 + 0.00548(c_{PV})_m] \tag{2}$$

in which $(c_{PV})_p$ and $(c_{PV})_m$ are weight percentages of the p- and m-divinylbenzene units incorporated in the copolymer by one vinyl only from the total content of divinylbenzene units. The dependence of the corrected absorbances ratios on the composition of the mixture is shown in Fig. 1.

Determination of the content of the divinylbenzene units incorporated in the copolymer by one vinyl is based on the measurement of the absorbances ratio A_{1630}/A_{795} (copolymers of m-divinylbenzene) and A_{1630}/A_{838} (co-
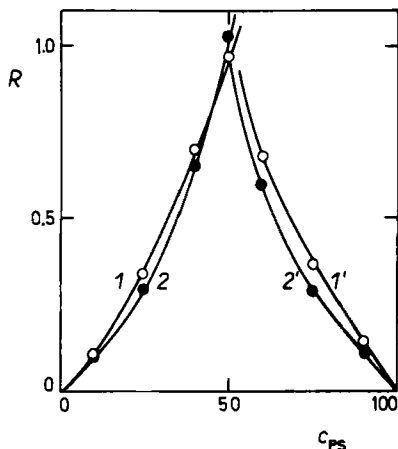
Fig. 1. Dependence of the absorbancy ratios on the composition of the polystyrene-polydivinylbenzene mixtures. c_{PS} wt-% of polystyrene, R values: (1), $(A_{760}/A_{838})_{cor}$; (1'), $(A_{838}/A_{760})_{cor}$; (2), $(A_{760}/A_{795})_{cor}$; (2), $(A_{795}/A_{760})_{cor}$.

polymers of p-divinylbenzene). For calibration, copolymers were used having a known content of pendant vinyl groups determined in the heterogeneous phase with mercuric acetate using polarometric indication. It has been established that the weight percentages of the p- and m-divinylbenzene units with pendant vinyls in the copolymer from the total content of the divinylbenzene units, $(c_{PV})_p$ and $(c_{PV})_m$, are given by the linear relationships

$$(c_{PV})_p = 175.0(A_{1630}/A_{830}) \tag{3}$$

$$(c_{PV})_m = 154.0(A_{1630}/A_{795}) \tag{4}$$

The problem of stability of the pendant vinyls during isolation and analysis was investigated on soluble copolymers of styrene and divinylbenzene. The measurements were carried out in solution, film, and KBr pellets, and the results showed that during the time needed for drying and measurements the relative content of pendant vinyl groups can decrease by 3% at most. This decrease in the content of the pendant vinyls was not taken into account when the samples were treated in a standard way.

The content of divinylbenzene units incorporated in the copolymer by both vinyl groups was calculated from the total content of the divinylbenzene units and from the fraction incorporated in the copolymer by one vinyl only.

RESULTS AND DISCUSSION

Dependence of the Composition of the Copolymer on Conversion

Divinylbenzene is a symmetric divinyl monomer: the analysis of the co-polymer composition at conversions up to 2-3% yielded copolymerization parameters for styrene (1) and the vinyl in divinylbenzene (2) (Ref. 2): $r_1 = 0.54$, $r_2 = 0.58$ for m-divinylbenzene and $r_1 = 0.15$, $r_2 = 1.22$ for p-divinylbenzene, which indicates that the vinyl group in p-divinylbenzene is more reactive that in m-divinylbenzene (cf. also Ref. 1). However, reactiv-ities of the vinyl groups in divinylbenzene are dependent; after one vinyl group of divinylbenzene has reacted, the reactivity of the remaining (pendant) vinyl group changes (falls). This is indicated by a change in the position of the absorption bands in the UV region [9]. The vinyl groups in m- and p-divinylbenzene absorb at 305 or 314 nm, respectively, whereas the pen-dant vinyls in both m- and p-divinylbenzene units absorb at 297 nm. This means that the pendant vinyl groups have the same reactivity, evidently close to that of the vinyl group in styrene. Since the pendant vinyls (com-ponent 3) are first formed and then disappear, the system is to be considered from the viewpoint of copolymerization of a ternary one with the copolymer-ization parameters $r_{12} = 0.15$, $r_{21} = 1.22$, $r_{13} = 1$, $r_{31} = 1$, $r_{23} = 1.22$, $r_{32} = 0.15$ (p-divinylbenzene) or $r_{12} = 0.54$, $r_{21} = 0.58$, $r_{13} = 1$, $r_{31} = 1$, $r_{23} = 0.58$, $r_{32} = 0.54$ (m-divinylbenzene). A general case of copolymerization of a monovinyl monomer and a divinyl monomer with dependent reactivities of vinyl groups was discussed elsewhere [10]. Since $r_{12}r_{23}r_{31} = r_{21}r_{32}r_{13}$, the composition of both copolymers and monomers is given by a system of differential equations [10]

$$\frac{dM_1}{dM_2} = \frac{r_{12}M_1(M_1 + M_2/r_{12} + M_3/r_{13})}{2r_{21}M_2(M_1/r_{21} + M_2 + M_3/r_{23})} \tag{5}$$

$$\frac{dM_3}{dM_2} = \frac{r_{32}M_3(M_1/r_{31} + M_2/r_{32} + M_3)}{2r_{23}M_2(M_1/r_{21} + M_2 + M_3/r_{23})} - \frac{1}{2} \tag{6}$$

$$dm_1/dm_2 = 2(dM_1/dM_2) \tag{7}$$

$$dm_3/dm_2 = 2(dM_3/dM_2) + 1 \tag{8}$$

$$dm_1 + dm_2 + dm_3 = -(dM_1 + dM_2 + dM_3) = M^\circ d\alpha \tag{9}$$

where M_1, M_2, and M_3 are numbers of moles of the vinyls in the monovinyl monomer, divinyl monomer, and pendant vinyl groups, respectively; m_1, m_2, and m_3 are numbers of moles of reacted units of the monovinyl monomer, reacted first vinyl groups in the divinyl units, and reacted pendant vinyl groups, respectively; M^0 is the number of moles of all vinyl groups at the beginning of the reaction; and α is the molar conversion of all vinyl groups. As has been shown [10], the above system can be solved numerically and yields the dependence of the integral composition of the copolymer and the composition of monomer on conversion.*

Figures 2 and 3 show the dependence of the divinylbenzene units, incorporated in the copolymer by one or both vinyls, on conversion for various initial compositions. The points correspond to infrared data. The molar conversion of the vinyl groups, α, was recalculated to the weight conversion, α_w, using the relationship

$$1 - \alpha_w = (1 - \alpha)[\epsilon_1 f_1 + (1 - \epsilon_1)f_2]/[\epsilon_1 f_1^0 + (1 - \epsilon_1)f_2^0] \qquad (10)$$

in which $f_1 = M_1/(M_1 + M_2 + M_3)$, $f_2 = M_2/(M_1 + M_2 + M_3)$, $\epsilon_1 = u_1/(u_1 + u_2/2)$, and u_1 and u_2 are the molecular weights of styrene and divinylbenzene, respectively, and values with the superscript ^{0} correspond to the initial composition. It can be seen that the content of the divinylbenzene units incorporated in the copolymer by both one or two vinyl groups is lower than the calculated value. Such negative deviations would not disappear even if the pendant vinyl groups had the same reactivity as the vinyl groups in divinylbenzene.

Deviations from the assumed copolymerization behavior become still more pronounced for the fraction of pendant vinyl groups. It can be clearly seen from Fig. 4 that in the initial stages of copolymerization the fraction of the pendant vinyls rapidly falls below the calculated values, whereas at high conversions the copolymers contain a large excess of the pendant vinyls. A considerable fraction of pendant vinyl groups remains in the copolymers after completion of copolymerization, when all monomers have been exhausted. These deviations increase with increasing content of divinylbenzene in the system.

Besides the analysis of the composition of the copolymer, the composition of monomers extracted from the gel was also analyzed, using gas chromatog-

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*The system of Eqs. (5)-(9) was solved numerically using a National Elliot 4130 computer.
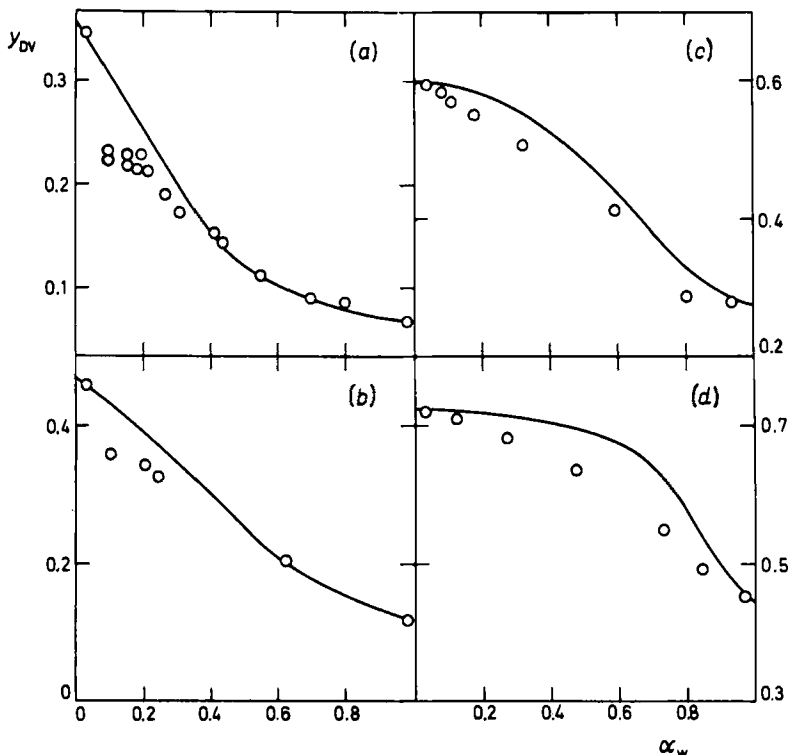
Fig. 2. Mole fraction of all p-divinylbenzene units incorporated in the co-polymer, y_{DV}, and dependence on the weight conversion, α_w. Content of p-divinylbenzene (wt-%): (a) 8, (b) 15, (c) 30, (d) 50. Curves are calcula-ted dependencies.

raphy. Figure 5 shows that in this case the deviations of experimental and calculated values are rather small.

The gel point conversions in dependence on concentration of divinylben-zene and dilution are summarized in Tables 1 and 2. The critical cross-linking density at the gel point depends on the weight-average degree of polymeriza-tion of "primary" chains, $\bar{P}_w$ (i.e., of chains which would arise by severing all cross-links), according to [11]
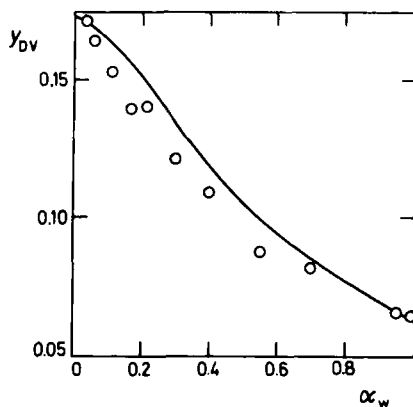
$$\rho_c = 1/\bar{P}_w \qquad (11)$$

Fig. 3. Mole fraction of all m-divinylbenzene units incorporated in the co-polymer, y_{DV}, and dependence on the weight conversion, α_w. Content of m-divinylbenzene: 8 wt-%. The curve is the calculated dependence.

and ρ is given by

$$\rho = 2m_3/(m_1 + m_2 + m_3) \tag{12}$$

because reaction of each pendant vinyl group produces two cross-linked units. The gel point conversion ought to fall with increasing concentration of the divinyl monomer and increasing reactivity of its vinyl groups. However, Eq. (11) was derived on the assumption that there is no intramolecular cross-linking and the system is homogeneous. The results in Tables 1 and 2 demonstrate that the critical conversion is higher by an order of magnitude than that calculated according to Eqs. (11) and (12) if values obtained for polystyrene polymerized under identical conditions are used for $\overline{P}_w$. Even more remarkable is the independence or an indication of a minimum on the curve α_{wg} vs. concentration of divinylbenzene, and also the fact that at a high content of divinylbenzene the more reactive p-isomer yields higher α_{wg} than the less reactive m-divinylbenzene. This inversion from lower to higher α_{wg} values for the p-isomer compared with the m-isomer, which is observed at increasing concentration of divinylbenzene (Table 1), also takes place at increasing dilution of the system with an inert solvent, while the concentration of divinylbenzene is kept constant (Table 2).

The gel point data for lower percentages of divinylbenzene are in keeping with the equilibrium degrees of swelling of gels isolated during copolymerization (Fig. 6), which characterize the degree of cross-linking in the gel [11].
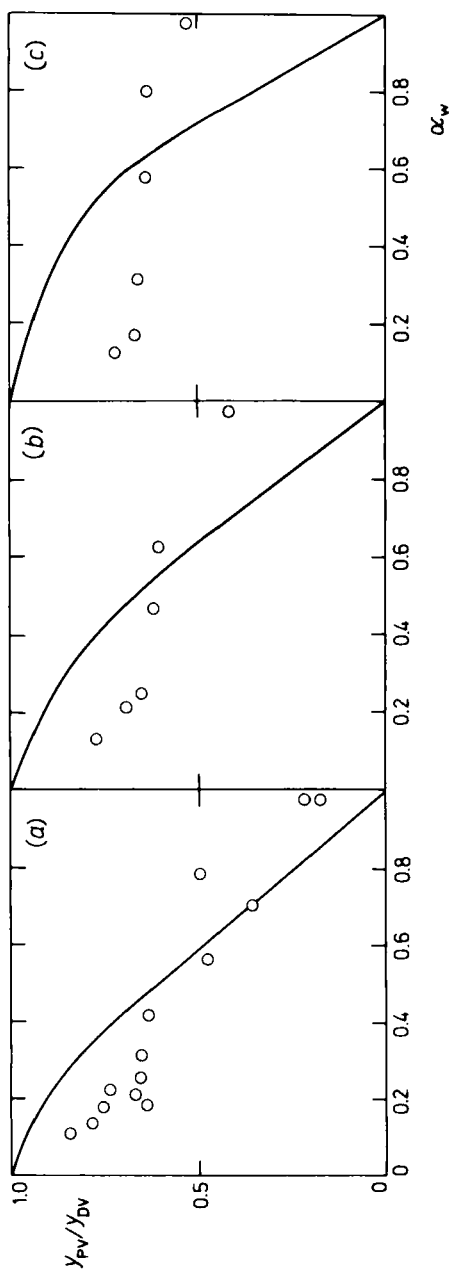
Fig. 4. Fraction of the p-divinylbenzene units with a pendant vinyl group of the total amount of divinylbenzene units incorporated in the copolymer and dependence on weight conversion. Content of p-divinylbenzene in wt-%: (a) 8, (b) 15, (c) 30. Curves are calculated dependencies.
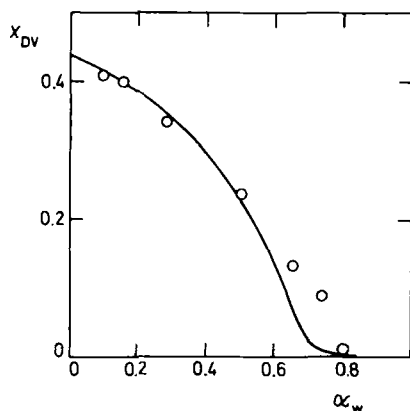
Fig. 5. Mole fraction of divinylbenzene in the monomer, x_{DV}, and dependence on weight conversion during copolymerization of styrene with 50% p-divinylbenzene. The curve is the calculated dependence.

Table 1. Effect of the Concentration of Divinylbenzene (DVB) on Critical Gel Point Conversion[a]

c_d[b]	α_{wg}[c]	
	p-DVB	m-DVB
1	13.2	14.1
10	4.4	4.9
20	3.5	3.3
50	3.6	3.6
70	3.6	3.4
100	3.6	3.3

[a]Copolymerization initiated with 0.3% dibenzoyl peroxide at 70°C,
[b]Wt-% of divinylbenzene,
[c]Critical gel point conversion in wt-%.

Table 2. Effect of the Diluent (Toluene) on Critical
Gel Point Conversion[a]

| | α_{wg}[c] | | | |
| | 8% DVB | | 15% DVB | |
φ_1[b]	p-DVB	m-DVB	p-DVB	m-DVB
0	5.3	5.5	4.4	4.7
0.1	5.5	5.5	5.3	4.8
0.2	5.6	5.8	5.8	5.1
0.3	5.9	5.8	6.0	5.6
0.4	–	6.6	6.2	5.7
0.5	7.2	7.2	7.8	7.5
0.6	8.8	8.8	10.5	9.4
0.8	19.7	18.7	24.5	21.3

[a]Copolymerization initiated with 0.3% dibenzoyl peroxide at
70°C,
[b]Volume fraction of toluene in monomers at the beginning
copolymerization,
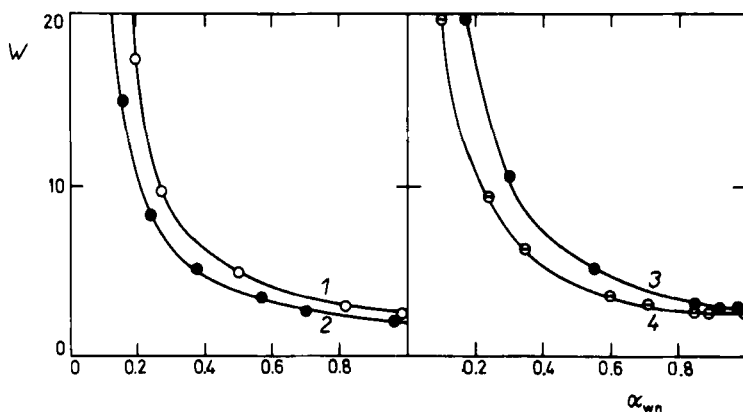[c]Critical conversion at gelation in wt-%.

Fig. 6. Decrease in the weight swelling degree of gels isolated during copo-
lymerization of styrene with m- and p-divinylbenzene and dependence on the
weight conversion of monomers to a cross-linked (insoluble) polymer. Di-
vinylbenzene content: (1) 4% m-DVB, (2) 4% p-DVB, (3) 15% m-DVB, (4)
15% p-DVB. α_{wn} conversion to the insoluble gel.

It is obvious that at a concentration of divinylbenzene of 4-15% the degrees of swelling of gels cross-linked with p-divinylbenzene are always lower, which indicates that at the same polymerization conversion these gels contain more cross-linked units.

Thus the copolymerization behavior of the divinylbenzenes with styrene and the network formation exhibit a number of deviations from the behavior based on the assumption of the independence of the copolymerization parameters of conversion or homogeneity of the system. These deviations can be summarized as follows:

(a) A slightly lower content of all divinylbenzene units incorporated in the copolymer, which is particularly easy to see at lower and medium conversions, and which is more pronounced in the case of the p-isomer.

(b) A lower content of pendant vinyl groups at lower conversions and their unexpectedly high content at high conversions.

(c) Independence (or indication of a minimum) of the gel point conversion on the concentration of divinylbenzene instead of the expected decrease.

(d) The fact that at a higher content of divinylbenzene or higher dilution the gel point conversion is higher for the p-isomer, which would seemingly correspond to a higher reactivity of the vinyl group in m-divinylbenzene.

To explain the observed deviations, it should be borne in mind that a decrease in the number of vinyl groups of a given type and the formation of cross-links depends not only on their reactivity, but also on their local concentrations. The growing macroradical comes into contact not only with the monomer molecules but also with pendant vinyls, a part of which is attached to the already formed portion of the chain. At low conversions, however, the concentration of the pendant vinyl groups in the domain of the growing chain is higher than their average concentration in the system, and the probability of their reaction with the radical is affected by the conformational statistics of the chain. The increased local concentration of the pendant vinyl groups leads to the formation of intramolecular connections. In cyclic and branched structures the relative reaction probability for pendant vinyl groups increase further so that at low conversions these compact formations can already have not only a low content of pendant vinyl groups but also a low content of monomers. This is why in these stages of copolymerization the content of pendant vinyls is lower than expected. The probability of participation of the pendant vinyl groups in a local reaction increases with concentration of the divinyl units in the chain, that is, with increasing per-

centage of the divinyl monomer and with increasing reactivity of its vinyl groups.

The lower content of all divinyl units incorporated in the copolymer (Figs. 2 and 3) is probably connected with the diffusion-controlled supply of monomers to the growing macroradical into the sphere of the compact coil. If in this case the propagation is faster than the supply of monomers from the outside, the divinyl monomer is used up more rapidly, and the un-reacted monomers are enriched with the monovinyl monomer; as a conse-quence, the content of the divinyl units in the polymer is lower. In the ex-treme case of the total local exhaustion of monomers, the copolymer formed would have the same composition as a copolymer obtained at full conversion of all vinyl groups. No such deviations from the assumed course can be ob-served for the composition of monomers, since at low conversions the amount of the copolymer is low in comparison with the amount of the mon-omers.

The tendency toward locally inhomogeneous copolymerization can also cause an abnormal dependence of the gel point conversion on the concen-tration and reactivity of vinyl groups in divinylbenzene. An inert diluent does not practically affect the local concentration of the pendant vinyl groups, but lowers the concentration of the monomers, so that the partic-ipation of pendant vinyl groups in the intramolecular reaction increases com-paratively.

The high content of pendant vinyl groups in the final stages of copolymer-ization is related to the reduced mobility of segments as a consequence of the formation of a densely cross-linked network and approach to the main transi-tion region. The fraction of pendant vinyl groups increases with increasing concentration of the cross-linking agent; it is evident that such diffusion-con-trolled "freezing" can happen not only in the whole system on attaining higher copolymerization conversions, but also locally at those points where compact polymeric formations have been formed and where the copolymer-ization has occurred to higher degrees. The existence of "frozen" vinyl groups has been observed earlier [12], and also with some other copolymers [13, 14].

It seems, therefore, that the main cause of the anomalies observed lies in the inhomogeneous course of the vinyl-divinyl cross-linking copolymerization.

REFERENCES

[1] R. H. Wiley, W. K. Mathews, and K. F. O'Driscoll, *J. Macromol. Sci.,* **A1**, 503 (1967).
[2] J. Malinský, J. Klaban, and K. Dušek, *Collect. Czech. Chem. Commun.,* **34**, 711 (1969).
[3] R. H. Wiley, J. K. Allen, S. P. Chang, K. E. Musselman, and T. K. Venkatachalam, *J. Phys. Chem.,* **68**, 1776 (1964).
[4] R. H. Wiley and T. K. Venkatachalam, *J. Polym. Sci., Part A,* **3**, 1063 (1965).
[5] R. H. Wiley and J. T. Badget, *J. Macromol. Sci.,* **A2**, 103 (1968).
[6] D. H. Freeman, *NBS Tech. Note No.* **509**, Washington 1970.
[7] B. T. Storey, *J. Polym. Sci., Part A,* **3**, 265 (1965).
[8] J. Klaban, V. Novák, and J. Malinský, *Allgem. Prakt. Chem.,* **19**, 321 (1968).
[9] D. J. Worsfold, J. D. Zilliox, and P. Rempp, *Can. J. Chem.,* **47**, 3379 (1969).
[10] K. Dušek, *Collect. Czech. Chem. Commun.,* **34**, 1891 (1969).
[11] P. J. Flory, *Principles of Polymer Chemistry,* Cornell Univ. Press, Ithaca, New York, 1953.
[12] K. Dušek, *Collect. Czech. Chem. Commun.,* **27**, 2841 (1962).
[13] J. C. H. Hwa, *J. Polym. Sci.,* **58**, 715 (1963).
[14] A. R. Shultz, *J. Amer. Chem. Soc.,* **80**, 1854 (1958).