Network Formation During Styrene-Divinylbenzene Copolymerization Investigated by the Fluorescence Polarization Method

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Presented at the 7th IUPAC Discussion Conference "Polymer Networks", Karlovy Vary, CSSR, September 15–19, 1980

Summary

If styrene–divinylbenzene copolymerization is performed at certain conditions of network formation, regions of relative high segmental density may occur. The segmental density can be monitored directly by the microstructure sensitive fluorescence polarization method. Measurements were made in the pre- and post-gel state at various degrees of conversion depending on the initial composition of the reaction mixture. The results, particularly in situations of high crosslinker content support the currently used models of network formation mechanisms during crosslinking copolymerization.

Introduction

The properties of networks depend on their structure and thereby on the peculiar process of network formation. The molecular network morphology is determined by the parameters of the reaction components (composition of the initial system, functionality and reactivity of the components) as well as by reaction pathways and kinetics of the crosslinking reaction. There are several factors which may be responsible for structure heterogeneity of polymer networks during polymerization (e.g., dilution by inert solvents, fixation of radicals at the growing network, and phase separation). The appearance of structural homogeneous networks seems to be more an exception than a rule. This is especially true for styrene–divinylbenzene copolymerization which has been intensively studied in the recent decades for academic and practical reasons (WILEY 1964, STOREY 1965, DUSEK 1967, MALINSKY 1971, AMBLER 1977, SCHWACHULA 1979, HEITZ 1979, DUSEK 1980).
The existing deviations from the theory of polyfunctional polymerization reaction (FLORY 1953, GORDON 1976) are related with the different reactivity coefficients, formation of intramolecular crosslinks (cyclization) and sterical hindrance (shielding) which result in the formation of densely crosslinked particles which are less densely linked externally and form the gel (DUSEK 1980). Thus, in principle, styrene–divinylbenzene type networks possess inhomogeneities with regard to the segmental densities. The existence of such inhomogeneities modifies the relation between crosslinking density and degree of swelling (FLORY-HUGGINS-theory, c.f. CHOQUET 1978). On the other hand, a microstructure sensitive method, like

the fluorescence polarization method, should be used to test the
network formation theories and one should correlate the "microsco-
pic" data (short-range, high frequency) with the "macroscopic" data
(long-range, low frequency) to clarify the conditions under which
inhomogeneous networks are formed. The discussion deals with three
main topics:

1. Behavior of the short-range property at the pre-gel to post-gel
   state transition.
2. Influence of conversion on the short-range property.
3. Influence of different initial compositions of reaction mixtures.

Experimental

Polymer networks were prepared by radical copolymerization using
styrene (St) and technical grade divinylbenzene (DVB)* in solution
(benzene) with 9-vinylanthracene (9-VA) as fluorescence indicator
and benzoyl peroxid (BPO) as initiator at 60° C. The initial compo-
sitions of the actually tested systems are given throughout the text.

To ensure that no significant changes in sequence length distribu-
tion and composition of the copolymers has been introduced by the
presence of the indicator (usually 10^{-4} mol/l), calculations were
made using the reactivity ratios and mole fractions of the compo-
nents St, DVB and 9VA (BRANDRUP 1975).

The samples for fluorescence polarization (FP) measurements were
prepared by stopping the polymerization with hydrochinone. They
were extracted for several hours with benzene at 25° C.

The apparatus for FP-measurement has been described elsewhere
(FUHRMANN 1976). The degree of polarization p $[\%]$ is defined as

$$p = \frac{I_{\|} - I_{\perp}}{I_{\|} + I_{\perp}} * 100 \; [\%] \tag{1}$$

where $I_{\|}$ and $I_{\perp}$ are the intensities of horizontally and vertically
polarized components of the fluorescence light. The correlation of
p with segmental density can be shown by the PERRIN-equation

$$(\frac{100}{p} - \frac{1}{3}) = (\frac{100}{p_o} - \frac{1}{3}) \; (1 + \frac{3\tau_f}{\varsigma}) \tag{2}$$

where ς is the average rotational relaxation time of the labelled
polymer segments which depends on the local frictional coefficient
of the kinetic unit (approximately 5 - 7 monomers), τ_f is the
fluorescence lifetime (4.5 ns), and p_o is the fundamental degree
of polarization (30 %) in the absence of rotational motion.

To investigate the local accessibility of polymer segments for
small molecules quenching experiments were made with the FP-appa-
ratus. The total intensity of fluorescence light was measured in
the quenched and unquenched state. The relations used for inter-
pretation are the STERN-VOLLMER-equation

$$I_o/I = 1 + k_q \tau_{fo} \; [Q] \tag{3}$$

and the SMOLUCHOWSKI-equation

$$k_q = 4\pi \sigma_{FQ} \; N_L \; (D_F + D_Q) \; \gamma \tag{4}$$

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* MERCK: 35 % p-DVB, 11 % m - DVB, 54 % ethylvinylbenzene

For further details see FUHRMANN 1980.

Results and Discussion

1. Pre-gel to post-gel transition

An example of network formation in solution is given in Fig.1 where, in the pre-gel state, the apparent molecular weight $\overline{M}_{wapp}$ (from GPC-data using the calibration curve of linear PS) and, in the post-gel state, the equilibrium volume degree of swelling Q_v are plotted versus the conversion time t.
The initial composition of the system and the reaction conditions are given in the caption. The same type of curves (without the p-values) were recently found by OKHASA 1979.

The additional information we can present is the relation between conversion time and segmental density characterized by the short-range dependent degree of polarization p (Eqn.2). Comparing the p-values of the first precursor at t=1h in the pre-gel state with that of linear molecules of the same molecular weight, one can see an enhancement in p due to branching. As the reaction continues the segmental density stays at a certain level while the molecules mere-ly grow ($\rightarrow$ increasing $\overline{M}_{wapp}$). In the post-gel state the segmental density rises only if the volume degree of swelling has reached a certain limit (in this case approx.10).
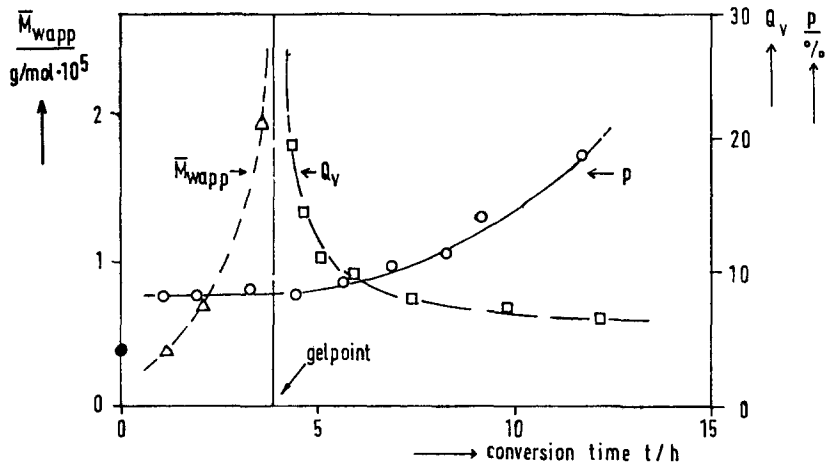

Fig.1: Molecular weight $\overline{M}_{wapp}$ ($\triangle$), equilibrium volume degree of swelling Q_v ($\square$) and degree of polarization p (o) as function of conversion time t (T=60 °C, solvent: benzene, composition 48,66 wt% St, 2.43 wt% DVB, 2.27% BPO). The $\overline{M}_{wapp}$ (●) and p-value (4%) of a linear molecule is included for reasons of comparison. (The p-values in the pre-gel state were measured with 0.1 wt% polymer in benzene solution.)

From the forgoing information it is not possible to confirm whether the network becomes more homogeneous in the course of reaction. However, this can be done by comparing networks with different

histories. The network with the lower p-value at the same degree of swelling would be the more homogeneous. This subject will be discussed in connection with Fig.5 in part three of this paper.

By investigating the network precursors in the pre-gel state, using the quenching experiment, one gets information about the molecular accessibility of the labelled polymer segments. In Fig.2 the STERN-VOLLMER-plot of solutions of the precursors and two "model"-polymers is shown.
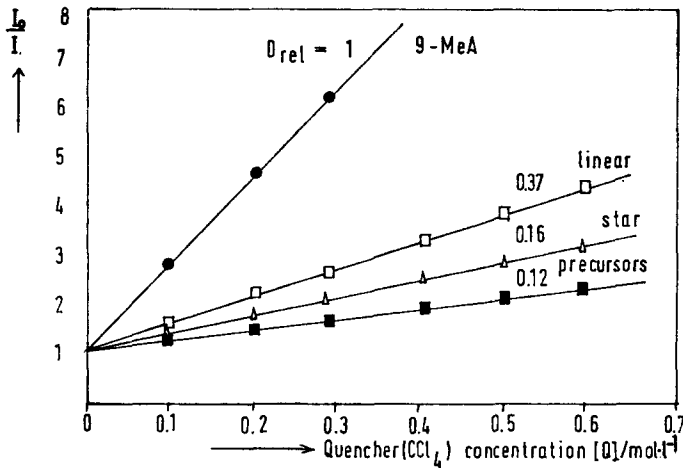

Fig.2: STERN-VOLLMER plot of solutions of 9-MeA (10^{-4} mol/l), linear PS ($\bar{M}_w = 10^5$ g/mol, 0.1 wt%), star polymer* (0.1 wt%) and the pre-gel "network-precursor" (0.1 wt%), solvent: benzene, T=25°C.

Applying the SMOLUCHOWSKI-equation (Eqn.4) to the experimentally evaluated k_q-values of the STERN-VOLLMER-equation (Eqn.3) and using 9-methylanthracene (9-MeA) as a reference, one gets relative translational diffusion coefficients.

Both the rotational diffusion (p-value (8%), see Fig.1) and the translational diffusion (D_{rel}-values, see Fig.2) are reduced in the precursors with respect to the linear molecules. An intermediate result is obtained for the star polymer* which is a model for a network junction where the indicator is located on the "surface" of the crosslink nodule by reaction.
The data given in Fig.2 for the three precursors fall on the same line. This is a further support for the conclusion (see discussion of Fig.1) that the precursors merely grow.

2. Influence of conversion on the short-range property

In Fig.3 the degree of polarization p and the equilibrium volume degree of swelling Q_v are plotted for selected systems (composition,

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* $\bar{M}_\eta$ linear: 9.21×10^4 g/mol, functionality f=11.2

see Tab.I) versus the conversion time t. The gel-points shift with
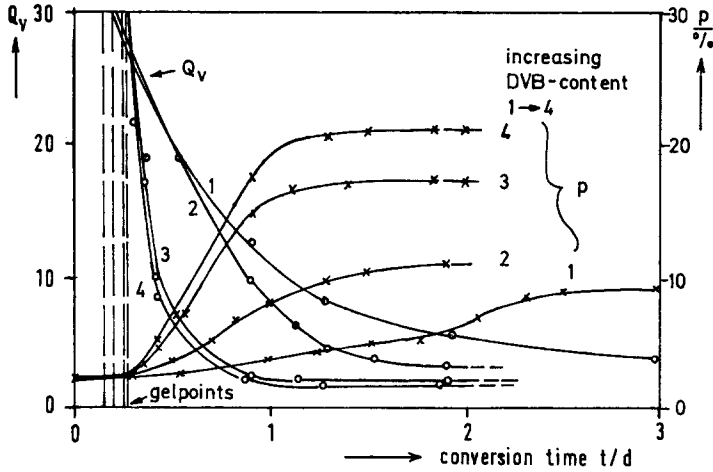increasing content of biunsaturated monomer and the highest con-

Fig.3: Volume degree of swelling Q_v and degree of polarization p
versus conversion time t (T=60 $^{\circ}$C, solvent: benzene; for
the system in Tab.I)

Table I: Initial composition of the systems (variation of DVB
content)

No.	St mol/l	DVB mol/l	BPO mol/l	Benz. mol/l	Gelpoint t(h)
1	3.94	0.160	$7.86 \cdot 10^{-3}$	5.64	≈ 7.0
2	./.	0.319	./.	./.	≈ 6.5
3	./.	0.638	./.	./.	≈ 5.0
4	./.	0.942	./.	./.	≈ 4.0

version rate is observed for the highest DVB content. In the same
way, the Q_v-values decrease fastest (OKHASA 1979) as the p-values
increase. As conversion is one important factor determining the
molecular architecture due to the unreacted double bonds (MALINSKY
1971, SHAH 1980), Fig.4 gives the data of Fig.3 versus conversion.

It is clearly demonstrated that with increasing conversion the
length of the elastically active network chains decreases and the
highest segmental densities are reached at relative high con-
versions. Especially in the case of the lowest DVB-content (curve 1),
drastic changes in Q_v and p can be observed at conversions beyond
60 %. This means that generally unreacted double bonds can still
react at high conversions increasing the network density. As a
consequence, the segmental mobility is reduced and locally compact
polymeric regions are formed (MALINSKY 1971). A comparison of the

p-values at same Q_v-values reveals small differences in segmental densities for the used systems.
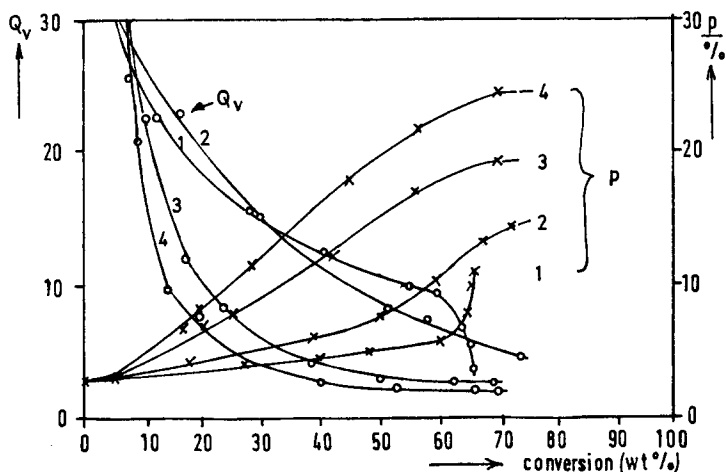

Fig.4: Relation between the volume degree of swelling Q_v, the degree of polarization p and conversion (systems as in Fig.3)

Table II: Initial composition (mol/l) of the systems (variation of St, DVB, BPO, Benz.)

comp. / most varied	St	DVB	BPO	Benz.	9-VA
St	0.731 <u>7.73</u> 5.650	0.532 0.205	$1.31 \cdot 10^{-2}$ $5.07 \cdot 10^{-3}$	9.42 3.64	$1.67 \cdot 10^{-4}$ $6.45 \cdot 10^{-5}$
DVB	4.090 3.571	0.072 <u>13.10</u> 0.942	$8.15 \cdot 10^{-3}$ $7.11 \cdot 10^{-3}$	5.85 5.11	$1.04 \cdot 10^{4}$ $9.09 \cdot 10^{5}$
BPO	3.956 3.874	0.319 0.312	$4.14 \cdot 10^{-4}$ <u>18.6</u> $7.73 \cdot 10^{-2}$	5.65 5.55	$1.0 \cdot 10^{-4}$ $1.0 \cdot 10^{-4}$
Benz.	6.674 2.261	0.532 0.212	$1.31 \cdot 10^{-2}$ $5.23 \cdot 10^{-3}$	1.81 <u>3.99</u> 7.51	$1.67 \cdot 10^{-4}$ $6.67 \cdot 10^{-4}$

The marked elements within each row contains the case of the most varied initial concentrations. The ratio between the upper and the lower limit of concentration is given for illustration (underlined). The rows of Table II show the initial compositions of the investigated systems.

The difference in local segmental densities will be demonstrated more clearly in part three of this paper where the initial con-

centrations of the other components are also varied.

3. Consideration of initial composition

The resulting networks are characterized by the plots (p versus Q_v) in Fig.5, which clearly show different segmental densities at equal Q_v-values.

The following general aspects of network formation discussed in the literature (DUSEK 1979, 1980, KAST 1979) can be evidenced by these experimental results:

- a high content of crosslinker gives rise to internally densely crosslinked particles which resemble microgels whose relative dense cores are linked together (variation of DVB and St content).

- dilution of the system supports intramolecular contacts and raises segmental density (solvent content variation, i.e.,Benz. content).

- lowering the degree of polymerization of the primary molecules (equivalent to the kinetic chain length of the radical homopoly- merization) improves the homogeneity (variation of BPO, except at high BPO content).

From the above considerations one can conclude that the most homo- geneous networks under the special features of styrene-divinyl- benzene copolymerization are those with the lowest p-value at a given Q_v-value.
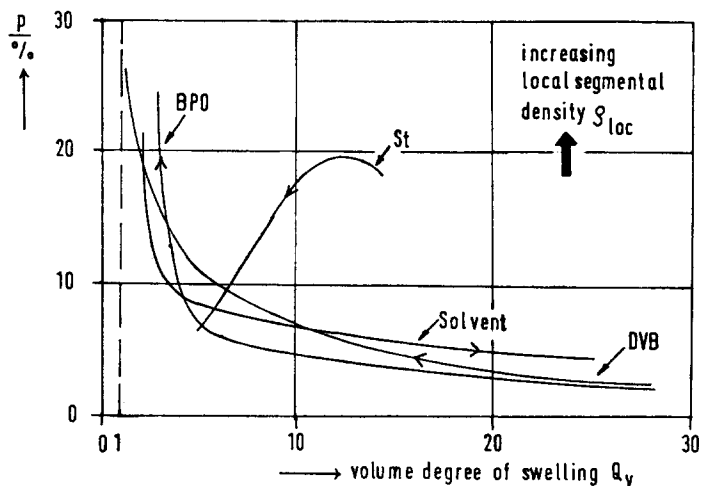

Fig.5: Relation between the degree of polarization p and the volume degree of swelling Q_v. The curves show the influence of different initial reaction mixtures by increasing (———►—) the fraction of one component (composition see Tab. II, T=60 °C, t=24 h)

Conclusions

Pre-gel state and transition to post-gel state

Branched molecules formed in the early stages of reaction generate

network inhomogeneities which can be investigated by the FP-method.
The special systems in Figs.1 and 2 show:
- no drastic change of the short-range dependent property p at the
  transition point whereas the long-range properties do.
- reduced molecular accessibility of segments in the network pre-
  cursors in contrast to linear molecules due to branching.

Post-gel state

Effect of conversion:
- the pendant double bonds formed during copolymerization can react
  up to the very late stages of the conversion and thereby reduce
  the length of the elastically active networks chains (decreasing
  Q_v) and the segmental mobility (increasing p).

Effect of initial composition:
- pendant double bonds in relative dense regions of high segmental
  density become less accessible for the reaction as the crosslinker
  content increases.
- network inhomogeneities are clearly revealed at high initiator,
  solvent, or low monofunctional monomer content comparing the
  different p - at the same Q_v-values.

Consequently the microstructure sensitive FP-method is able to dis-
tinguish between networks of different segmental inhomogeneities
and allows decisions which network is the more homogeneous.

References

AMBLER C. and MCINTYRE D.: J. Appl.Polym.Sci. 21, 2269 (1977)
BRANDRUP J. and IMMERGUT E.H., Ed.: Polymer Handbook, J. Wiley,
New York, 1975
CHOQUET M. and RIETSCH F.: Polymer 19, 513 (1978)
DUSEK K.: Collect. Czech.Chem.Commun. 32, 1182 (1967)
DUSEK K.: Makromol.Chem., Suppl. 2, 35 (1979)
DUSEK K. et al.: Polymer Bull. 3, 19 (1980)
FLORY P.: Principles of Polymer Chemistry, Cornell Univ. Press,
Ithaca, 1953
FUHRMANN J. and HENNECKE M.: Coll.Polym.Sci. 254, 6 (1976)
FUHRMANN J. and LEICHT R.: Coll.Polym.Sci. 258, 631 (1980)
GORDON M. and TEMPLE W.B.: in Chemical Application of Graph Theory,
A.T. Balaban, Ed., Academic Press, New York, 1976
HEITZ W.: Angew.Makromol.Chem. 76/77, 273 (1979)
KAST H. and FUNKE W.: Makromol.Chem. 180, 1335 (1979)
MALINSKY J. and KLABAN J.: J.Macromol.Sci., Chem. A-5, 1071 (1971)
SCHWACHULA G.: Z.Chem. 18, 242 (1978)
STOREY B.T.: J.Polym.Sci. A-3, 265 (1965)
OKHASA R. et al.: Eur.Polym.J. 15, 975 (1979)
WILEY R.: J.Phys.Chem. 68, 1776 (1964)