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Heterogeneities of styrene-divinylbenzene-copolymers

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SUMMARY

The heterogeneity of copolymers of styrene and divinylbenzene was investigated. The distribution of divinylbenzene units within the crosslinked copolymer yields information about the inhomogeneity of the network formed. Proceeding from the monomer reactivity ratios, the monomer compositions and from the conversion we set up histogramms of the distribution of the divinylbenzen-isomers within the formed copolymers. As a mathemathical expression of heterogeneity we used the relative variance. Possibilities to influence the heterogeneities found are discussed.

INTRODUCTION

Poly(styrene-co-divinylbenzene) is the basis for the production of ion exchange resins. The structure of these copolymers plays an essential role for the properties of the ion exchangers produced out of them, s. e. g. SCHWACHULA and POPOV (1982).

Our observations rested primarily upon kinetic investigations of the radical and anionic statistic copolymerization as well as anionic block copolymerization of the system styrene-divinylbenzene.

For the statistic copolymerizations the monomer reactivity ratios were determined and on this basis qualitative statements on the structure were made. In the present contribution the heterogeneity should be quantitatively dealt with by means of a computer-based analysis.

EXPERIMENTS

Styrene and divinylbenzene were copolymerized and the decrease of monomer concentration was followed up by gas chromatography, POPOV and SCHWACHULA (1979). The monomer reactivity ratios were determined and compared by various methods. Unknown values for further monomers were borrowed from the literature or calculated. The analysis of the heterogeneity was accomplished by the following monomer reactivity ratios for the radical system styrene-divinylbenzene, POPOV and SCHWACHULA (1981 a).

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1) Styrene/2)p-divinylbenzene
$r_{12} = 0{,}65$ $r_{21} = 1{,}10$ (experiment)

1) Styrene/3)m-divinylbenzene
$r_{13} = 0{,}54$ $r_{31} = 0{,}98$ (experiment)

2) p-divinylbenzene/3)m-divinylbenzene
$r_{23} = 0{,}88$ $r_{32} = 1{,}11$ (calculated)

1) Styrene/4)acrylonitrile
$r_{14} = 0{,}41$ $r_{41} = 0{,}04$
(mathematical mean value by YOUNG (1966)

2) p-divinylbenzene/4)acrylonitrile
$r_{24} = 1{,}44$ $r_{42} = 0{,}37$ (calculated)

3) m-divinylbenzene/4)acrylonitrile
$r_{34} = 1{,}78$ $r_{43} = 0{,}36$ (calculated)

For determining the heterogeneity a computer KRS 4200 was used. The programme was written in DIWA.

RESULTS

The chemical heterogeneity is manifested qualitatively in the change of the chemical composition of the copolymer in the course of the copolymerization. The reason for it are the various monomer reactivities. This involves a more or less inhomogeneous incorporation of cross-link components in the copolymer. A quantitative expression is given by the distribution of the amounts of the cross-linking agent in the polymer mixture after completing the polymerization.
As numerical value the variance or the ratio of the variance to the maximum possible variance is suitable for characterizing the heterogeneity. This ratio is referred to as relative variance by us. The variance is analogous to the heterogeneity parameter Q according to BUSHUK and BENOIT (1958). Q has an equal value to the variance, multipled by the mean molecular weight of the polymer. Since the numerical value of the variance yields only an insufficient information, it is necessary to set up e. g. a histogram for characterizing the polymer.
For this purpose a polymer is subdivided into classes according to its content of a component (chemically approximate uniform fractions) and the ratio between the amount of substances of these classes and the total amount of substances is considered. In the present case we consider the component divinylbenzene in the styrene-divinylbenzene-copolymers. Thus, a histogram of distribution is being obtained. The function formed hereby indicates the distribution of the cross-linking agent and in this way distribution of the cross-linkage points.
As a basis of the calculation served a system of differential equations of the type

$$MP_i(C) = M_i(C) - \frac{dM_i(C)}{dC} \cdot (1 - C)$$

Here

$M_i = M_i(C)$	mole fraction of the component i in the monomer mixture at the conversion C
$MP_i = MP_i(C)$	mole fraction of the component i of a monomer incorporated in the polymer at a certain moment (conversion) = the amount of the component i in the polymer being just formed
C	conversion

For this system a solution for two arbitrary monomers was found by MEYER and LOWRY, 1965. We applied the same system to any number of monomers and established the corresponding calculating programme.

Input:

n	number of all monomers;
k	number of the monomers whose distribution in polymers should be expressed;
c	interval for the rise of conversion (mole per cent);
C_e	final conversion (%);
$M_{01} \ldots M_{0n}$	amount of the components in the monomer feed (mole per cent);
$S_i \ldots S_k$	extent of the class for the components i to k for calculating the histogram (mole per cent);
(r_{ij})	monomer relativity ratios in matrix form

Output:
the copolymerization diagram (C, $M_i(C)$, $MP_i(C)$);
the histogram of the distribution for the components i to k in table form;
the boundaries of the classes (mole per cent);
the relative abundance (% of the polymer in the class mentioned);
variance = (%);
relative variance (r.v.);
"density" D. It serves as a figure for the graphic evaluation and indicates the height of the column in the respective class in the histogram. It is defined as:

$$D = \frac{n_i}{n_t \cdot b_i}$$

n_i	amount of substances of the polymers of the class i
n_t	total amount of substance
b_i	extent of the class i.

If required, the distribution of the sum obtained from the amounts of several components may be expressed, e. g. the distribution of p-divinylbenzene + m-divinylbenzene in the polymer. In Fig. 1 and 2 there are histograms of the distribution of p-divinylbenzene and m-divinylbenzene resp. in the polymer composed of 8 mole per cent divinylbenzene and 92 mole per cent styrene at a 100 % conversion.

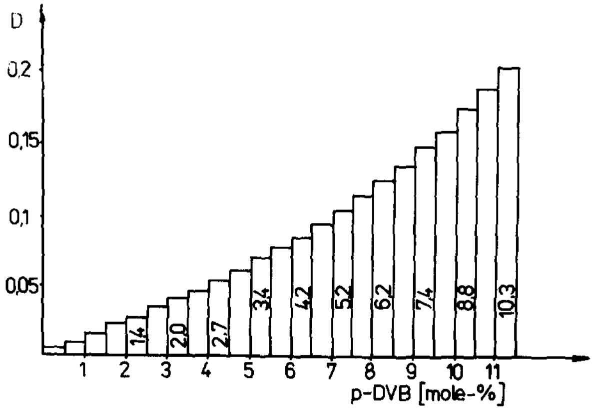

Fig. 1: Histogram of the distribution of p-divinylbenzene (8 mole per cent) in the poly(styrene-co-p-divinylbenzene) r.v. 9,61 • 10^{-3}.

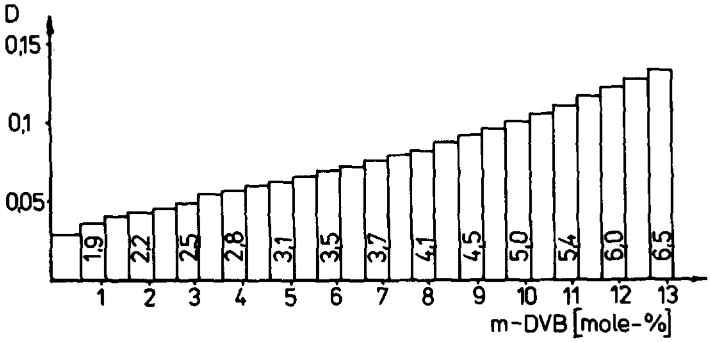

Fig. 2: Histogram of the distribution of m-divinylbenzene (8 mole per cent) in the poly(styrene-co-m-divinylbenzene) r.v. 17,36 • 10^{-3}.

The heterogeneity of the distribution of divinylbenzene in the poly(styrene-co-m-divinylbenzene) was found to be larger than that in the poly(styrene-co-p-divinylbenzene) (r.v. 17,36 • 10^{-3} resp. 9,61 • 10^{-3}). If a third comonomer acrylonitrile is put in the amount of 2 or 8 or 10 mole per cent, the homogeneity in the poly(styrene-co-p-divinylbenzene) (Fig. 3) improves and the relative variance decreases: 8,01 • 10^{-3} resp. 5,65 • 10^{-3} resp. 3,90 • 10^{-3}. Analogous to it the heterogeneity in the poly(styrene-co-m-divinylbenzene) (Fig. 4) and the relative variance 15,09 • 10^{-3} resp. 11,42 • 10^{-3} resp. 8,43 • 10^{-3} decrease.

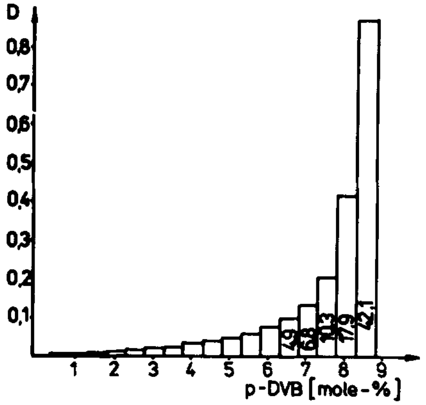

Fig. 3: Histogram of the distribution of p-divinylbenzene (8 mole per cent) in the poly(styrene-co-p-divinylbenzene-co-acrylonitrile).
ACN 10 mole per cent, r.v. 3,90 • 10^{-3}.

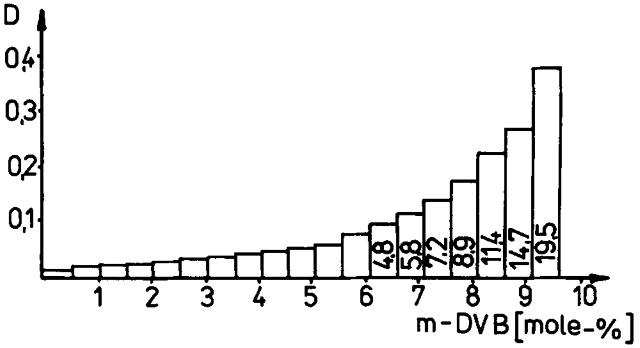

Fig. 4: Histogram of the distribution of m-divinylbenzene (8 mole per cent) in the poly(styrene-co-m-divinylbenzene-co-acrylonitrile).
ACN 10 mole per cent, r.v. 8,43 • 10^{-3}

Also in a copolymer of styrene, p-divinylbenzene, m-divinylbenzene and acrylonitrile the relative variance 7,25 • 10^{-3} shows that the heterogeneity is relativelly small (Fig. 5)

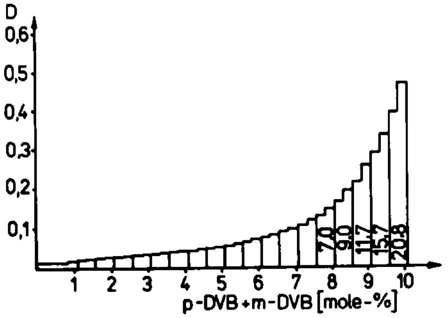

Fig. 5: Histogram of the distribution of divinylbenzene (p-divinylbenzene + m-divinylbenzene = 8 mole per cent in ratio 1 : 4) in the copolymer of styrene, divinylbenzene and acrylonitrile, ACN 10 mole per cent, r.v. 7,25 • 10^{-3}.

The results presented show that the addition of acrylonitrile improves the homogeneity of the distribution of the cross-linking units, whereas the same system without acrylonitrile indicates the relative variance 15,4 • 10^{-3}. This statement was confirmed by the testing of some properties of the ion exchange resins produced out of them, SCHWACHULA and POPOV (1982).

REFERENCES

BUSHUK, W. and BENOIT, H., Can. J. Chem. 36, 1616 (1958)
MEYER, V.E. and LOWRY, G.G., J. Polm. Sci. A 3, 2843 (1965)
POPOV, G. and SCHWACHULA, G., Plaste Kautsch. 26, 374 (1969)
POPOV, G. and SCHWACHULA, G., Plaste Kautsch. 28, 312 (1981 a)
POPOV, G. and SCHWACHULA, G., Plaste Kautsch. 28, 372 (1981 b)
SCHWACHULA, G. and POPOV, G., Pure Appl. Chem. 54, 2103 (1982)
YOUNG, L.J. in: Polymer Handbook, New York, WILEY and SONS 1966, p. 341

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