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Polymeric photosensitizers: 3. Determination of the copolymerization parameters for *N*-vinylcarbazole and sodium styrenesulfonate

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Sodium styrenesulfonate (SSS)–*N*-vinylcarbazole (VCz) copolymers were synthesized and characterized. The reactivity ratios for the monomers were determined as $r_{VCz} = 1.0 \pm 0.1$ and $r_{SSS} = 10.8 \pm 0.8$. Distribution of the monomers in sequences of various length was estimated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: copolymers; sodium styrenesulfonate; *N*-vinylcarbazole)

INTRODUCTION

There is a growing interest in a development of the new types of water-soluble polymers. Recently, several water-soluble polymeric photocatalysts have been synthesized and intensively studied[1–6]. The polymers are constructed from hydrophilic and hydrophobic units. In the aqueous solutions macromolecules adopt the conformation which enables solubilization of sparingly water-soluble molecules. The hydrophobic units display the ability to absorb the light from the n.u.v.–visible spectral region. The energy of the absorbed light can be used to induce photochemical reaction with participation of the molecule of solubilized compound[2,3,7]. The properties of these polymers are strongly dependent on their composition. It is well known that the copolymer characterized by a defined composition can be obtained if one knows the reactivity ratio for the pair of the monomers used in polymerization.

The aim of this work was determination of the reactivity ratios for the pair of the monomers: sodium styrenesulfonate (SSS) and *N*-vinylcarbazole (VCz) in free radical polymerization leading to formation of water-soluble copolymers and estimation of the distribution of the monomer units in sequences of various length.

EXPERIMENTAL

Materials

Sodium styrenesulfonate (SSS, Monomer-Polymer & Dajac Laboratories, Trevase, USA) was purified by recrystallization from 19/1 (v/v) mixture of methanol and water at 60°C and dried under vacuum. *N*-Vinylcarbazole (VCz, Fluka, Buchs, Switzerland, pure) was twice crystallized from methanol at 40°C and dried in a vacuum oven. *N*-Ethylcarbazole (EtCz, pure, Aldrich, Milwaukee, USA) was recrystallized twice from ethanol and once from an ethanol–water mixture. 2,2′-Azobis (isobutyronitrile) (AIBN, pure, POCH, Gliwice, Poland) was purified by crystallization from ethanol at 40°C and dried under vacuum. Poly(sodium 4-styrenesulfonate) (PSSS, Aldrich, Milwaukee, USA) was dissolved in water, dialysed and freeze-dried.

Methanol (pure, POCH), ethanol (pure, POCH), dimethyl sulfoxide (DMSO, pure, Aldrich), 1-butanol (pure, POCH), dichloromethane (for h.p.l.c., Aldrich, Milwaukee, USA) were used without further purification.

Table 1 The compositions of the polymerization mixtures and *N*-vinylcarbazole (VCz) content in the copolymers determined by different methods

Sample	Molar feed ratio $n_{VCz}:n_{SSS}$	VCz content in the copolymers [mol %] i.r.	u.v./vis[a]	n.m.r.	Elemental analysis
P1	5:95		0.5	–[b]	
P2	10:90		0.9	1.4[b]	1.2[c]
P3	20:80		2.5	2.8	2.7[c]
P4	30:70		5.2	5.4	
P5	40:60	8.5			
P6	50:50	14.7			
P7	55:45	19.0			
P8	60:40	–	–	–	–
P5′	40:60 ($\gamma > 30\%$)	13.6			13.8[d]

[a] Calculations based on the extinction coefficient of the model compounds:
EtCz $\epsilon = 3631\ dm^{-3}\ cm\ mol$ at 331 nm in THF[11]
$\epsilon = 23\,800\ dm^{-3}\ cm\ mol$ at 262 nm in CH_2Cl_2[12]
PSSS $\epsilon = 403\ dm^{-3}\ cm\ mol$ at 262 nm in H_2O[13]
[b] Low precision
[c] Determined from C, S content in the polymers after ionic exchange
[d] Determined from C, N content in the polymer without ionic exchange

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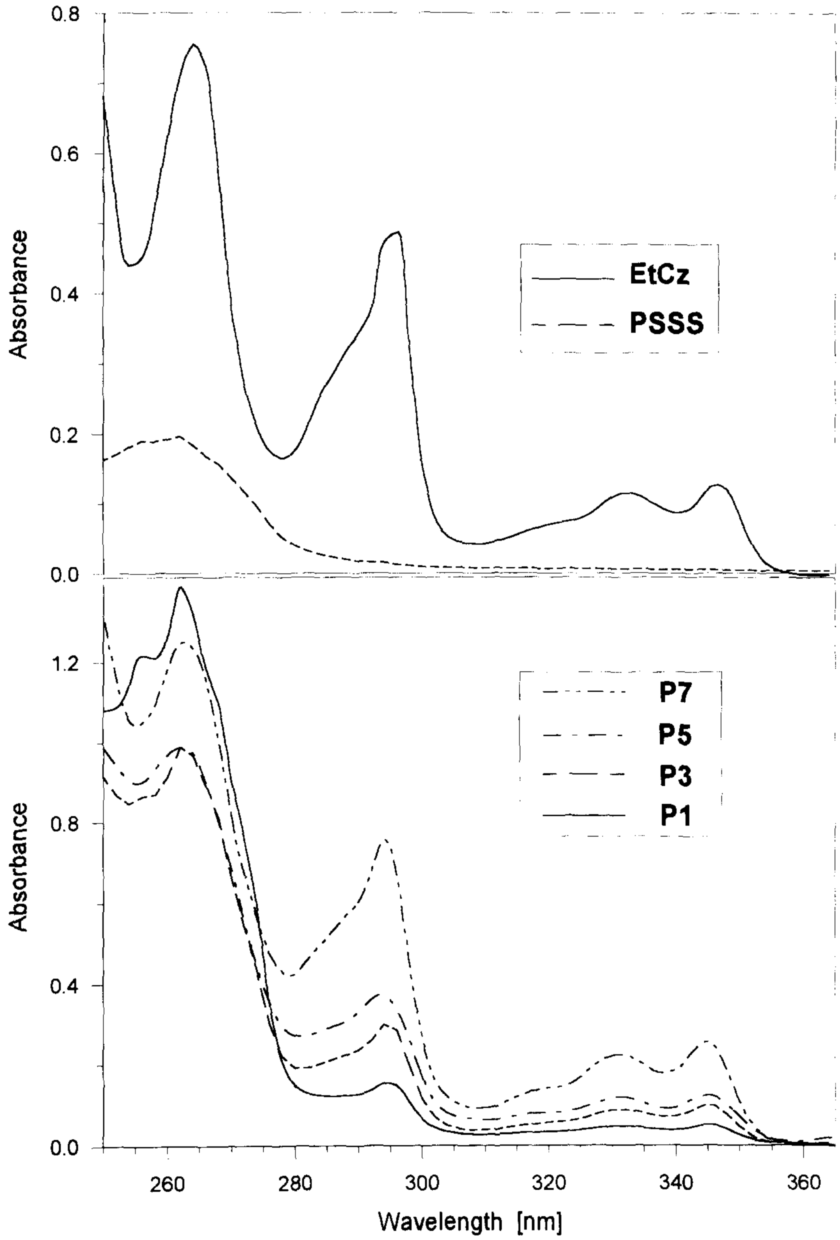

Figure 1 The electronic absorption spectra of EtCz (in dichloromethane), PSSS (in water) and selected PSSS–VCz polymers (in water)

Apparatus

U.v./vis. spectra. The u.v./vis spectra of the samples were obtained using a HP 8452A Diode-Array spectrophotometer.

I.r. spectra. The i.r. spectra were measured with use of Bruker IFS 48 spectrophotometer.

N.m.r. spectra. The ^{1}H n.m.r. spectra of the samples were measured using Bruker AMX 500 spectrometer.

Polymer synthesis

PSSS–VCz copolymers were synthesized and purified according to the previously described method[8]. The free radical polymerization of the mixture of monomers was carried out in degassed DMSO at 60°C. The reaction was initiated by AIBN. The samples, after polymerization, were precipitated with 1-butanol, filtered, washed three times with diethyl ether and dried in vacuum oven at 40°C. The resulting polymer was dissolved in water, exhaustively dialysed (Fisher, cellulose tubing, cut-off $12\,000$–$14\,000\,\mathrm{g\,mol^{-1}}$) against deionized water and freeze-dried. The composition of the reaction mixtures used for polymerization are shown in *Table 1*. The polymerization was terminated at a low degree of conversion ($\gamma < 5\%$) for all polymers (P1–P8) except of the polymer P5′ for which degree of conversion reached about 30%.

RESULTS AND DISCUSSION

Determination of the compositions of PSSS–VCz copolymers

It has been observed that polymerization of all monomer mixtures resulted in formation of polymers. However, the yield of the polymer formation decreases considerably with the increase in concentration of VCz in reaction mixture. All polymers, except for P8, are soluble

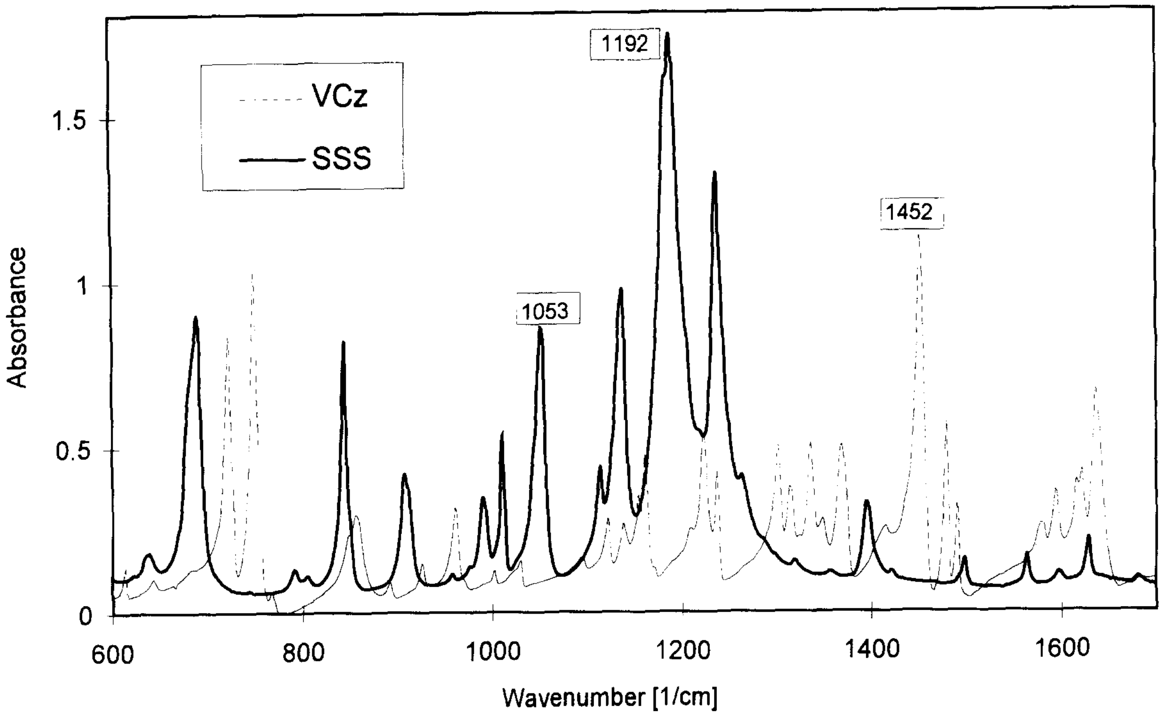

Figure 2 The i.r. spectra of the monomers in KBr pellets

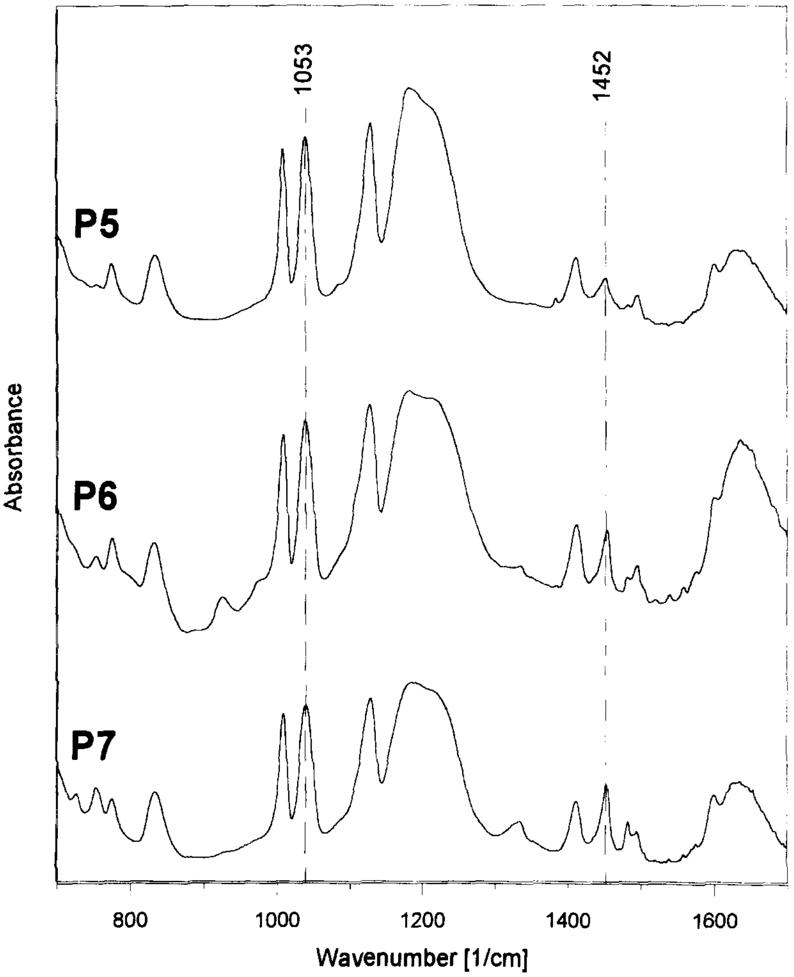

Figure 3 The i.r. spectra of selected polymers in KBr pellets

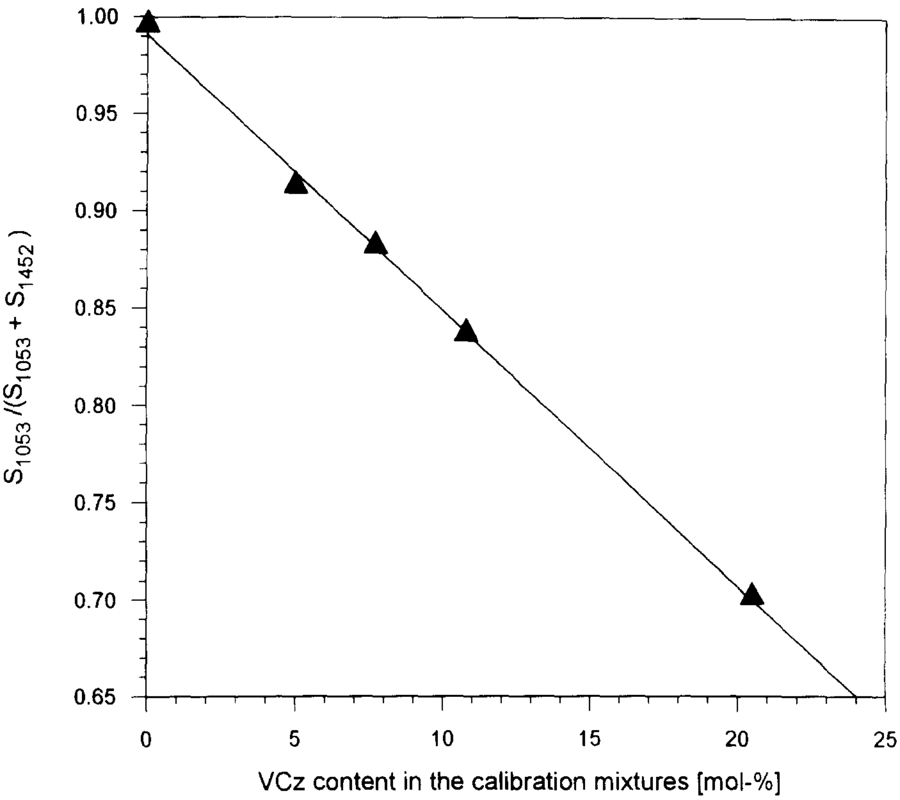

Figure 4 Calibration plot for the analysis of the i.r. spectra

in water up to several grams per litre. Polymer P8 displays limited solubility in water.

The compositions of the polymers have been determined using spectroscopic methods and the elemental analysis (see *Table 1*).

The PSSS–VCz copolymers with low Cz unit contents were characterized based on their u.v.-vis and n.m.r. (^{1}H) spectra. *Figure 1* shows the u.v.-vis absorption spectra for PSSS–VCz copolymers and the spectra of EtCz and PSSS, used as the model compounds. This method could be used to characterize the copolymers with a low carbazole content in the polymer chain. At higher concentration, the interactions between the chromophores led to the hypochromic effect. It has been shown that the molar extinction coefficients determined for the *N*-vinylcarbazole homopolymer[9] and for the copolymers with high content of Cz[10] are considerably lower than that for the model compound, EtCz (up to 40% at the 294 nm band).

The ^{1}H n.m.r. spectra of acceptable quality were obtained only for the PSSS–VCz with low content of carbazole up to about 5 mol%. The spectra for the polymers P1–P4 were measured in DMSO solutions. The respective spectra for PSSS (^{1}H n.m.r., D_2O); aromatic region, ($\delta = 6.2$–7.2, wide band and $\delta = 7.2$–8.0, wide band), and *N*-isopropylcarbazole[14] were used to perform the quantitative analysis of the PSSS–VCz copolymers. The spectra of the polymers with high concentration of Cz cannot be used for the quantitative analysis because of the strong interactions between Cz groups which induce significant changes in the spectra[14–16].

The compositions of PSSS–VCz copolymers (P2–P4) determined by u.v. and n.m.r. spectroscopy are in reasonably good agreement (see *Table 1*).

The compositions of the PSSS–VCz copolymers with higher VCz unit concentrations were determined based on their absorption spectra in the i.r. region. The spectra for polymers and monomers (VCz and SSS) were measured in KBr pellets (see *Figure 2* and *Figure 3*). The non-overlapping bands at 1452 cm^{-1}, which are characteristic for VCz (Ar frame) and at 1192 and 1053 cm^{-1}, which are characteristic for SSS ($-SO_3$ group) were chosen for the quantitative analysis. The ratios of the areas of the respective bands were calculated and the content of the VCz was determined from the calibration plot (*Figure 4*). The calibration plot was prepared using the spectral data for several monomer mixtures of known compositions. This method is limited to the polymers containing more than 5 mol% of VCz. For the polymers with lower concentration of VCz the quantitative analysis is difficult because of the high background produced by the SSS units.

The elemental analyses were carried out for chosen polymers after ionic exchange. It has been shown that in the presence of sodium counterions large amounts of inorganic sulfur-containing salts are formed during the analysis.

The results obtained from the elemental analysis carried out for a few chosen polymers are in very good agreement with those reached by the spectroscopic methods.

Determination of the reactivity ratios

The reactivity ratios for SSS (r_{SSS}) and VCz (r_{VCz}) have been determined based on our experimental data for the polymers P1–P7 and using two methods: Fineman–Ross[17] and Kelen–Tüdôs[18].

According to the Fineman–Ross method the reactivity ratios can be determined from the following

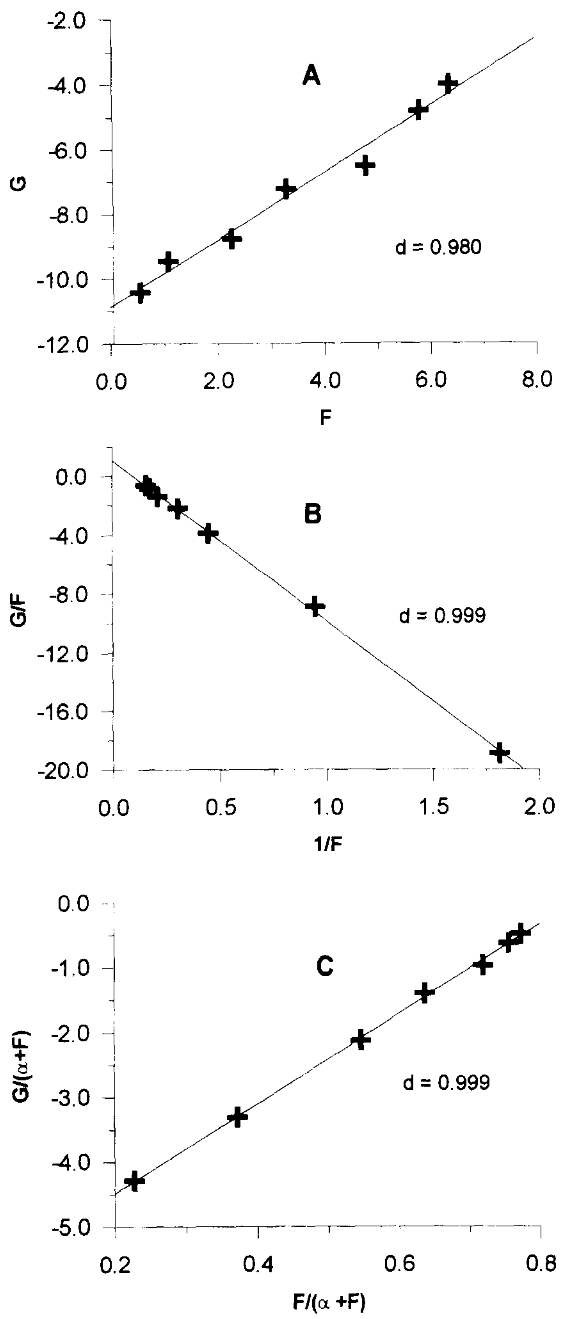

Figure 5 Plots used for determination of the reactivity ratios: (A) G vs F (according to equation (1)); (B) G/F vs $1/F$ (according to equation (2)); (C) $G/(\alpha + F)$ vs $F/(\alpha + F)$ (according to equation (3)). (The value d is the coefficient of determination in linear regression method)

equations:

$$G = r_1 \cdot F - r_2 \tag{1}$$

and

$$\frac{G}{F} = -r_2 \cdot \frac{1}{F} + r_1 \tag{2}$$

where:

$G = \dfrac{a(b-1)}{b}$

$F = \dfrac{a^2}{b}$

r_1, r_2, reactivity ratio

$a = \dfrac{M_1}{M_2}$, monomers molar ratio in the feed

Table 2 The reactivity ratios calculated with the Fineman–Ross and the Kelen–Tüdôs methods

	Fineman–Ross Eqn (1)	Fineman–Ross Eqn (2)	Kelen–Tüdôs Eqn (3)	Recommended values
r_{VCz}	1.0	1.1	1.0	1.0 ± 0.1
r_{SSS}	10.8	10.9	10.8	10.8 ± 0.8

Table 3 The values of parameters e, Q, r for monomers N-vinylcarbazole (VCz) and sodium styrenesulfonate (SSS)

Monomer	e	Q	r	Reference
VCz	−1.29	0.26	0.042	21
SSS	−0.59	2.49	14.5	22
VCz	−1.4	0.41	0.053	22
SSS	−0.59	2.49	9.79	22

$b = \dfrac{dM_1}{dM_2}$, which is equal to molar ratio of the copolymer components

In order to obtain the values of r_1 and r_2 with the same accuracy both equations (1) and (2) have been used. (It is known that in the linear regression method the value of an intercept can be determined more precisely than the value of a slope.)

The plots of G vs F and G/F vs $1/F$ give the reactivity ratios (see *Figure 5A*, *B* and *Table 2*).

The Kelen–Tüdôs method is based on the following equation:

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha}\right)\frac{F}{\alpha + F} - \frac{r_2}{\alpha} \tag{3}$$

where

$$\alpha = \sqrt{F_{\min} \cdot F_{\max}}$$

The reactivity ratios can be determined from the plot of the above equation (see *Figure 5C* and *Table 2*). The results obtained by both methods are almost the same. The reactivity ratio for SSS is very high. The dependence of carbazole content in copolymers on the concentration of VCz content in monomer feed is shown in *Figure 6*. The plot is typical for such a pair of reactivity ratios in which $r_1 \leq 1$ and $r_2 > 1$[19].

The values of r_{SSS} and r_{VCz} were also calculated using the Alfrey–Price semi-empirical method[20]. The method allows one to predict the reactivity ratios for a pair of monomers if values of two parameters, Q and e, are known and using the equations:

$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] \tag{4}$$

and

$$r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)] \tag{5}$$

The literature values of e and Q for VCz and SSS[21,22] and also the calculated values of reactivity ratios are shown in *Table 3*. It should be noted that the results obtained for PSSS–VCz copolymers by the semi-empirical method show considerable discrepancy from those obtained experimentally. The semi-empirical results can be disregarded because in using them one would not reproduce the experimentally determined composition of PSSS–VCz copolymer with high VCz content, e.g. 19 mol% at a low degree of conversion. Assuming the values of

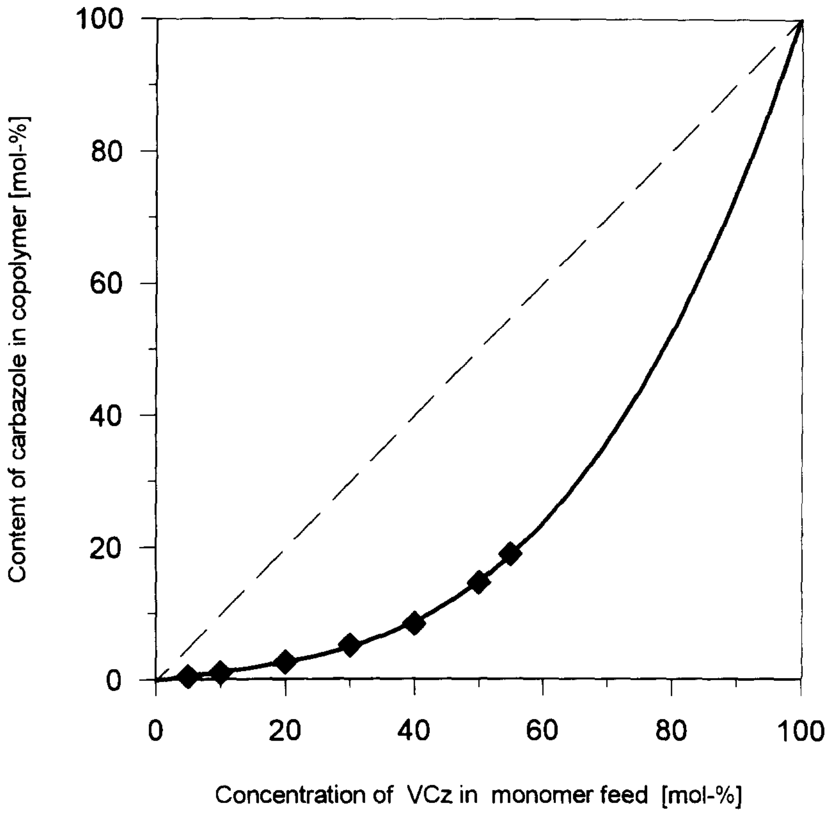

Figure 6 Variation of PSSS–VCz composition with monomer feed

Table 4 The values of reactivity ratios for monomers *N*-vinylcarbazole (VCz) and styrene (St)

r_{VCz}	r_{St}	Reference
0.012	5.5	22
0.026	5.93	21
0.032	5.72	21
0.062	5.6	24
0.08	4.5	25
0.02	5.17	26

the reactivity ratios shown in *Table 3* gives the value of VCz content, respectively, as 7.6 mol% and 10.6 mol% for the highest molar feed ratio (P7), which contradicts our experimental results.

The experimentally determined reactivity ratios suggest that the PSSS–VCz copolymers are built mainly from the long sequences of SSS separated by short sequences or isolated units of VCz. Statistical calculations verified this suggestion. Two parameters have been calculated: the statistical average length of the sequences of a given monomer, $\bar{n}$, and the probability of the sequence distribution, $P(n)$, according to the equations[23]

$$\bar{n}_1 = r_1 \cdot a + 1 \tag{6}$$

$$P_1(n) = \left(\frac{r_1 \cdot a}{r_1 \cdot a + 1}\right)^{n-1}\left(1 - \frac{r_1 \cdot a}{r_1 \cdot a + 1}\right) \tag{7}$$

The results are shown in *Figure 7*.

It would be interesting to compare the reactivity of VCz with SSS with the literature data for the copolymerization of VCz with styrene (S). The literature data on reactivity ratios for VCz and S are shown in *Table 4*. The reactivity of VCz appears to be considerably lower for copolymerization with S than with SSS. It is, however, very difficult to explain this effect by simply taking into account the presence of the sulfonate groups in SSS. One has to remember that the copolymerization of VCz with SSS was carried out in a polar solvent (DMSO) while all literature data for the VCz and S pair are determined in nonpolar solvents. Thus, it is difficult to separate the substituent effect and solvent effect. It has been shown that the increase in a polarity of the solvent results in increase of the reactivity parameter of the monomer by changing its resonance parameter Q[27].

CONCLUSIONS

Copolymerization of SSS with VCz in DMSO solution leads to the formation of water-soluble PSSS–VCz copolymers. The copolymers are generally richer in SSS than VCz. The reactivity ratios for the monomers were determined experimentally. It has been shown that the semi-empirical method cannot be used successfully to predict the reactivity ratios in the systems studied. The experimentally determined reactivity ratios and the statistical analysis of the sequence distribution indicate that the copolymer chains are formed from the long sequences of SSS separated by the short segments or isolated units of VCz.

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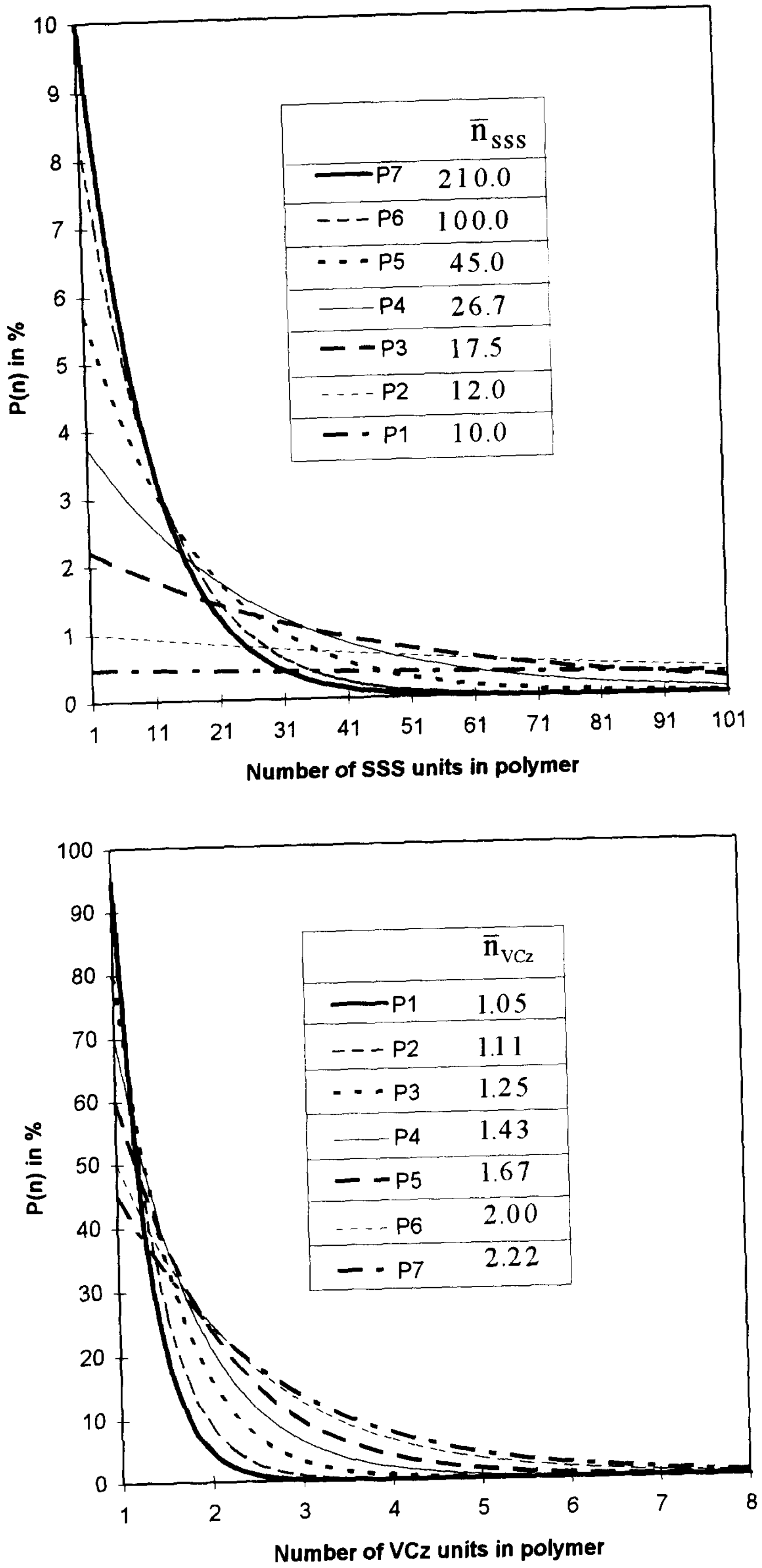

Figure 7 The VCz and SSS sequence distribution (equation (7)) and the average length of monomer units in the copolymers (equation (6))

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