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EVALUATION OF THE REACTIVITY RATIOS AND SEQUENCE DISTRIBUTION IN EPISULPHIDE COPOLYMERS BY ^{13}C NMR

CARLO CORNO, ARNALDO ROGGERO, TITO SALVATORI and
ALESSANDRO MAZZEI
Snamprogetti, Direzione Ricerca e Sviluppo, 20097 S.Donato Milanese, Milano, Italia

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Abstract—The microstructure (in particular the distribution of the monomeric units) has been determined by means of ^{13}C NMR for the three copolymers ethylene sulphide–propylene sulphide (ES–PS), ethylene sulphide–isobutylene sulphide (ES–IBS) and propylene sulphide–isobutylene sulphide (PS–IBS) prepared with anionic catalysts. Low and high conversion copolymers have been analysed. The results for the diad and triad fractions have been used for the evaluation of the reactivity ratios in the copolymerizations. The values are discussed and compared with those found using the Finemann and Ross method.

INTRODUCTION

A description [1] has already been given for the synthesis of episulphide based copolymers, in particular ethylene sulphide–propylene sulphide (ES–PS), ethylene sulphide–isobutylene sulphide (ES–IBS) and propylene sulphide–isobutylene sulphide (PS–IBS) with a particular type of anionic catalysts. Microstructure study of these polymers (tacticity, enchainment and monomeric unit distribution) was carried out using ^{13}C NMR. The spectra were discussed and interpreted; some considerations on the tacticity and chain arrangement have already been reported [2,3].

Quantitative aspects of monomeric unit distribution in polymers of low (5–20%) and high (80–100%) conversion have been dealt with in this paper. From the experimental data for the fractions of diads and triads, values of the reactivity ratios were obtained; they are discussed and compared with those obtained from application of the classical method of Finemann and Ross [4].

EXPERIMENTAL

Polymer synthesis was previously described [1]. The ^{13}C NMR spectra, their interpretation and the experimental conditions have already been reported [2,3].

The spectra were recorded on a Varian XL 100 instrument operating at 25.14 MHz in the Fourier transform (FT) mode. The FT conditions:

SPC WDT (Hz) = 1500
ACQ TIME (sec) = 2.6
PULS DLY (sec) = 2.4 (only in copolymers containing IBS)
PULS WD (μsec) = 20 (90° PW = 51 μsec)
K-TRANS = 5–10

ensured the complete relaxation of all the C carbons. The relative intensities of the peaks were measured by integration of the spectrum using the computer (integration method) or by cutting and weighing each band area in a Xerox copy of the spectrum (weighing method).

RESULTS

(a) Calculation of the sequence distribution

We will explain case by case the procedure for the calculation of the sequence fractions from the measurements of the peak areas in the ^{13}C NMR spectra. The backbone, in terms of triads, of the three copolymers is:

—C(I)—C(II)—S—C(I)—
C(II)—S—C(I)—C(II)—S—

and the methyl substitutions, because of the regular enchainment [2,3], are always on C(II).

(1) *ES–PS copolymers.* The assignments of the fourteen peaks are reported in Table 1. For calculation of the diad distribution, the procedure was as follows. Taking the total area of the peaks of the main chain as being equal to 1, i.e.

$$\sum_{i=1}^{13} S_i = 1,$$

the following can be obtained immediately:

$$S_1 + S_2 + S_3 + S_4 + S_8 = f_{PP} \qquad S_5 + S_6 + S_{13} = f_{PE}$$
$$S_7 + S_9 + S_{10} = f_{EP} \qquad S_{11} + S_{12} = f_{EE}$$

where S_i is the area of the *i*th peak and f is the sequence fraction.

The triad fractions have been normalized according to the nature of their central member.

The peaks numbered 9, 10, 11, 12 in Table 1 have been used for the calculation of the ES triads. The peaks 9, 10, and 11 belong to the second methylene carbon of the ES in the triads PEP, PEE, and EEP. The peak 12 is common to the two methylene carbon atoms. The fraction α of this peak belonging to the second methylene carbon is easily obtained however by subtracting from S_{12} the area which competes for the first methylene group of the EEP triads (evidently equal to S_{11}) and dividing the result by two.

Table 1. Assignment of the peaks in the ^{13}C NMR spectrum of the ES–PS copolymers

	Chemical Shift	Carbon	Assignments Monomer	Sequence	Diad
1	41.76	CH	P	PPP syndiotactic	
2	41.63	CH	P	EPP syndiotactic	PP
3	41.50	CH	P	PPP isotactic	
4	41.31	CH	P	EPP isotactic	
5	41.02	CH	P	PPE	PE
6	40.83	CH	P	EPE	
7	40.41	CH_2	P	EPP + EPE	EP
8	38.90	CH_2	P	PPP + PPE	PP
9	33.83	$CH_2(II)$	E	PEP	EP
10	33.67	$CH_2(II)$	E	EEP	
11	33.04	$CH_2(II)$	E	PEE	
12	32.92	$CH_2(II)$ $CH_2(I)$	E E	EEE EEE + EEP	EE
13	31.60	$CH_2(I)$	E	PEE + PEP	PE
14	20.98	CH_3	P	in all the sequences	

We therefore have

$$\alpha S_{12} = \frac{S_{12} - S_{11}}{2}$$

and the triad fractions are:

$$f_{PEP} = S_9 \quad f_{EEP} = S_{10} \quad f_{PEE} = S_{11} \quad f_{EEE} = \alpha S_{12}$$

with the condition

$$S_9 + S_{10} + S_{11} + \alpha S_{12} = 1.$$

For calculation of the fractions of the PS triads, the following procedure was used.

Taking the sum of the areas of the first six peaks as one, i.e. $S_1 + S_2 + S_3 + S_4 + S_5 + S_6 = 1$, we obtain directly

$$S_5 = f_{PPE} \quad S_6 = f_{EPE}.$$

As the single evaluations of the areas of the first four peaks are subject to considerable errors, we can assume the signals of the triads f_{PPE} and f_{EPP} to be equal [5], i.e. $S_2 + S_4 = S_5$.

Hence the f_{PPP} fraction can be obtained from the equation

$$f_{PPP} = S_1 + S_2 + S_3 + S_4 - S_5.$$

The values of the diad and triad fractions in the case of the six copolymers are reported in Table 2. The feed composition, conversion and copolymer composition are reported for each sample.

(2) *ES–IBS copolymers.* The assignments of the eleven peaks of the spectrum are reported in Table 3. For calculation of the triad fractions having isobutylene sulphide as the central monomeric unit, the sum of the three areas was taken as 1.

$$S_2 + S_3 + S_4 = 1$$

and immediately

$$S_2 = f_{EIE} \quad S_3 = f_{EII+IIE} \quad S_4 = f_{III}.$$

In order to calculate the diad distribution, noting that the peaks 10 and 11 originate from two methyl carbon atoms and therefore these areas must be

Table 2. Diad and triad fractions in ES–PS copolymers

	Feed mole-fraction of E	Composition mole-fraction of E	Conversion %	Diad distributions				ES triad fractions				PS triad fractions		
				f_{PP}	f_{PE}	f_{EP}	f_{EE}	f_{PEP}	f_{EEP}	f_{PEE}	f_{EEE}	f_{PPP}	$f_{PPE+EPP}$	f_{EPE}
1	0.10	0.145	40.1	0.747	0.119	0.111	0.023	0.769	0.076	0.115	0.040	0.740	0.245	0.015
2	0.15	0.283	12.6	0.503	0.207	0.211	0.079	0.525	0.207	0.195	0.073	0.480	0.438	0.082
3	0.20	0.230	70.5	0.595	0.166	0.172	0.067	0.503	0.212	0.216	0.069	0.614	0.319	0.067
4	0.25	0.377	18.8	0.376	0.235	0.238	0.151	0.409	0.201	0.210	0.180	0.367	0.504	0.134
5	0.30	0.310	90.1	0.468	0.205	0.211	0.116	0.401	0.239	0.234	0.126	0.512	0.405	0.083
6	0.35	0.355	98.0	0.408	0.213	0.222	0.157	0.340	0.236	0.228	0.196	0.421	0.426	0.150

Table 3. Assignment of the peaks in the ^{13}C NMR spectrum of the ES–IBS copolymers

	Chemical shift in ppm from TMS	Carbon	Assignments Monomer	Sequence	Diad
1	47.20	CH_2	I	EII + EIE	EI
2	46.61	C	I	EIE	
3	45.83	C	I	EII + IIE	
4	45.06	C	I	III	
5	41.77	CH_2	I	IIE + III	II
6	35.14	$CH_2(II)$	E	IEI	IE(or EI)
7	35.02	$CH_2(II)$	E	IEE(or EEI)	
8	33.30	$CH_2(I)$ $CH_2(II)$	E E	EEE + EEI (or IEE) + EEE + EEI	EE
9	29.45	$CH_2(I)$	E	IEE + IEI	IE
10	28.60	CH_3	I	III + EII (or IIE)	II
11	28.28	CH_3	I	EIE + IIE (or EII)	EI (or IE)

Table 4. Diad and triad fractions in ES–IBS copolymers

	Feed mole fraction of E	Composition mole fraction of E	Conversion %	Diad distributions			IBS triad fractions		
				f_{II}	f_{IE+EI}	f_{EE}	f_{III}	$f_{IIE+EII}$	f_{EIE}
1	0.08	0.19	17.6	0.659	0.313	0.028	0.665	0.294	0.051
2	0.25	0.38	12.9	0.356	0.508	0.136	0.375	0.453	0.172
3	0.58	0.58	6.3	0.173	0.514	0.313	0.178	0.470	0.352
4	0.30	0.37	85.0	0.429	0.418	0.153	0.510	0.352	0.138
5	0.40	0.46	89.8	0.320	0.455	0.225	0.399	0.407	0.194
6	0.50	0.56	90.5	0.231	0.229	0.340	0.391	0.532	0.257

divided by two to obtain the contribution of a single carbon atom, let us put

$$S_1 + S_5 + S_6 + S_7 + S_8 + S_9 + \tfrac{1}{2}S_{10} + \tfrac{1}{2}S_{11} = 1$$

obtaining

$$f_{EE} = S_8 \quad f_{II} = S_5 + \tfrac{1}{2}S_{10}$$
$$f_{IE+EI} = S_1 + S_6 + S_7 + S_9 + \tfrac{1}{2}S_{11}.$$

Even if from the areas of the peaks 6 and 7 it is possible to evaluate the fractions of the triads having ethylene sulphide as central unit, the difficulty of measuring separately the two areas has led us to put aside this calculation.

The values of the diad and triad fractions in the case of the six copolymers analyzed are reported in Table 4, showing also feed composition, conversion and copolymer composition.

(3) *PS–IBS copolymers.* The assignments of the twelve peaks of the spectrum are reported in Table 5.

As in the previous case, calculation of the fractions of the triads centred on IBS has been obtained taking the sum of the three areas as 1.

$$S_1 + S_2 + S_3 = 1$$

and therefore obtaining immediately

$$S_1 = f_{PIP} \quad S_2 = f_{PII+IIP} \quad S_3 = f_{III}.$$

For calculation of the diad fractions, use was made of the areas of the methyl carbon peaks, because of the overlapping of the signals of the main chain carbon atoms. Naturally the fact should be noted that the signals at 28.56 and 28.16 ppm are derived from two carbon atoms.

Therefore assuming

$$\tfrac{1}{2}S_9 + \tfrac{1}{2}S_{10} + S_{11} + S_{12} = 1$$

the following relationships are obtained:

$$\tfrac{1}{2}S_9 = f_{II} \quad \tfrac{1}{2}S_{10} + S_{11} = f_{IP+PI} \quad S_{12} = f_{PP}.$$

Table 6 shows the diad and triad fractions for the three copolymers, all at 100% conversion and therefore with compositions equal to those of the feeds.

(b) *Determination of the reactivity ratios according to the Finemann and Ross method*

We have calculated the reactivity ratios in the three copolymerizations with anionic catalysts already described [1], under the experimental conditions reported in Table 7. The values are:

(a) for the ES–PS copolymer from

$$y = r_{EP}x - r_{PE} \quad r_{EP} = 2.7 \quad r_{PE} = 0.46$$

and from

$$y' = r_{PE}x' + r_{EP} \quad r_{EP} = 2.4 \quad r_{PE} = 0.44$$

Table 5. Assignment of the peaks in the ^{13}C NMR spectrum of the PS–IBS copolymers

	Chemical shift in ppm from TMS	Assignments			
		Carbon	Monomer	Sequence	Diad
1	46.06	C	I	PIP	
2	45.46	C	I	PII + IIP	
3	44.82	C	I	III	
4	44.57	CH_2	I	PIP + PII	PI
5	42.02	CH	P	PPI + IPI	PI
6	41.20	CH CH_2	P I	IPP + PPP III + IIP	PP II
7	38.86	CH_2	P	PPP + PPI	PP
8	36.07	CH_2	P	IPP + IPI	IP
9	28.56	CH_3	I	III + PII (or IIP)	II
10	28.16	CH_3	I	PIP + IIP (or PII)	IP (or PI)
11	21.17	CH_3	P	IPI + IPP (or PPI)	IP (or PI)
12	20.91	CH_3	P	PPP + IPP (or PPI)	PP

Table 6. Diad and triad fractions in PS–IBS copolymers

	Feed mole fraction of P	Composition mole fraction of P	Conversion %	Diad distributions			IBS Triad fractions		
				f_{PP}	f_{PI+IP}	f_{II}	f_{PIP}	$f_{PII+IIP}$	f_{III}
1	0.35	0.35	100	0.129	0.462	0.409	0.130	0.435	0.435
2	0.40	0.40	100	0.170	0.482	0.348	0.185	0.455	0.360
3	0.60	0.60	100	0.397	0.478	0.125	0.334	0.462	0.204

Table 7. Mole fraction of the feed (M) and composition (m) of the copolymers used for the calculation of the reactivity ratios applying the Finemann–Ross equation

Copolymers		M_1	m_1*	Conversion
Type	Sample	mole fraction	mole fraction	%
ES_1–PS	1	0.40	0.619	11.6
	2	0.30	0.504	11.5
	3	0.20	0.353	14.7
	4	0.10	0.203	11.0
ES_1–IBS	1	0.10	0.228	11.0
	2	0.20	0.373	17.8
	3	0.30	0.557	18.4
	4	0.40	0.680	13.0
PS_1–IBS	1	0.80	0.815	21.0
	2	0.60	0.667	10.4
	3	0.40	0.490	20.7
	4	0.25	0.330	14.2

Other data: Monomers = 50 mmol; Solvents = THF + HEMPA (55 + 5 cm^3); Temp. = 25°C.

* Calculated by ^{1}H-NMR.

where

$$y = \frac{F}{f}(f-1);\ x = \frac{F^2}{f};\ y' = \frac{f-1}{F};$$

$$x' = \frac{f}{F^2};\ F = \frac{M_1}{M_2};\ f = \frac{m_1}{m_2}$$

and M_1, M_2 are the feed concentrations and m_1, m_2 are the copolymer compositions.

(b) For the copolymer ES–IBS from

$$y = r_{EI}x - r_{IE} \quad r_{EI} = 3.84 \quad r_{IE} = 0.48$$

and from

$$y' = r_{IE}x' + r_{EI} \quad r_{EI} = 3.14 \quad r_{IE} = 0.4.$$

(c) For the copolymer PS–IBS from

$$y = r_{PI}x - r_{IP} \quad r_{PI} = 0.99 \quad r_{IP} = 0.48$$

and from

$$y' = r_{IP}x' + r_{PI} \quad r_{PI} = 1.1 \quad r_{IP} = 0.57.$$

As is evident from the data of Table 7, it has not always been possible to investigate the whole range of composition owing to the insolubility of copolymers of high ES content.

Furthermore it has been difficult to keep the conversions at low values (10%). The data should therefore be considered indicative and useful for comparitive purposes.

(c) *Calculation of the reactivity ratios from the sequence distribution measurements*

The Harwood program [6,7] was used for calculation of the reactivity ratios using the data on diad and triad fractions. This program, in its original version, enables the calculation of the copolymer composition and of the diad and triad distributions from the feed composition, the conversion and the reactivity ratios. Depending on the option of the operator, the calculations are based on either terminal or penultimate reactivity ratios and are applicable for either low or high conversion copolymers. For instantaneous copolymers, copolymer compositions are calculated from monomer reactivity ratios and from monomer feed concentrations by means of standard relationships [8].

For high conversion copolymers, these calculations are performed at various increments (0.05%), the monomer composition being adjusted continuously for monomer converted to polymer by means of an iterative routine.

In our case we have used this program as a subroutine in an optimization procedure introducing the feed and conversion data and going on to determine the values of the reactivity ratios which minimize the sum of the squares of the differences between the calculated and the experimental values of the diad and triad fractions.

The lack of a penultimate effect has been assumed and therefore the calculation was carried out for the ratios of terminal reactivity. The penultimate effect has been observed in only a few radical polymerizations [9] and in the copolymerization of monomers belonging to different classes [10] but never in the copolymerization of closely similar monomers. The hypothesis therefore that such an effect is not significant in our case appears to be reasonable.

The "*simplex*" method [11] has been used as minimization algorithm, the initial values from which to carry out the regression being both the values of r_A and r_B found with the Finemann and Ross method and the arbitrary values $r_A = 1$ and $r_B = 1$. The values obtained from both the regressions were identical, confirming that an absolute minimum had been reached.

On using the values of Tables 2, 4 and 6 the following reactivity ratios were found for the three systems:

ES–PS $r_1 = 2.12$ $r_2 = 0.461$ $r_1.r_2 = 0.977$
ES–IBS $r_1 = 2.98$ $r_2 = 0.347$ $r_1.r_2 = 1.034$
PS–IBS $r_1 = 1.44$ $r_2 = 0.640$ $r_1.r_2 = 0.922$

DISCUSSION

The reported products of the reactivity ratios can be considered without any doubt to be unity within experimental error. It can therefore be expected that for instantaneous copolymers or at low conversions, diad and triad fraction values are very near those of a perfectly random copolymer. Obviously at high conversion deviation from random distribution, with prevalent homopolymeric sequence, can be expected;

Table 8. Standard deviations from the random model

	High conversion		Low conversion	
ES–IBS	6.055	10^{-3}	0.282	10^{-3}
ES–PS	1.116	10^{-3}	0.421	10^{-3}
PS–IBS	0.411	10^{-3}	–	--

the greater the ratio r_1 r_2, the greater will be the deviation.

This deviation will therefore lie in this sense

$$\text{ES–IBS} > \text{ES–PS} > \text{PS–IBS}.$$

This is confirmed in quantitative terms by calculation of the standard deviations between the experimental results of diad and triad fractions and the values calculated for a polymer of the same composition having a perfectly random distribution. The standard deviations for the three copolymers are reported in Table 8.

These data clearly show the trend of the deviation of the different copolymers from the random distribution and the considerable decrease of the standard deviations for the low conversion copolymers. In this latter case, the standard deviations are very near the experimental error (0.2–$0.4 \cdot 10^{-3}$).

A second observation can be made on the found reactivity ratios. As is known [12], if the reactivity ratios of the two binary systems with a common monomer are known, and the reactivity ratios for the combination of the remaining two comonomers are required, then the following equation is valid

$$\frac{r_{13}}{r_{31}} = \frac{r_{12} \cdot r_{23}}{r_{21} \cdot r_{32}}$$

which, in our case, since $r_{ij} \cdot r_{ji} = 1$, becomes

$$r_{EI} = r_{EP} \cdot r_{PI} \qquad r_{IE} = r_{IP} \cdot r_{PE}.$$

The calculated values of $r_{EP} \cdot r_{PI} = 3.05$ and $r_{IP} \cdot r_{PE} = 0.295$ appear in reasonable agreement with the experimental values of r_{EI} and r_{IE}.

The reactivity ratios found with the Finemann and Ross method are not far from those found from the sequence analyses; they differ slightly in absolute values, but the order is still

$$r_{ES} > r_{PS} > r_{IBS}.$$

Some data on the reactivity ratios of episulphide copolymers synthesized with different anionic catalysts have already been reported [13] and the reactivity order found was

$$r_{ES} > r_{PS} = r_{IBS}.$$

It should be remembered that the reactivity ratios in ionic copolymerizations depend strongly on the experimental conditions and therefore a strict comparison is not possible. It can be stated however that the values of the reactivity ratios found by us agree well with the basicity data reported [13] for the three episulphide monomers; a higher reactivity in anionic polymerization is obviously related to a lower basicity. Evidently the steric factor does not play an important role because the opening of the episulphide ring, with anionic catalysts, occurs between the primary carbon and the sulphur [14].

CONCLUSIONS

The reactivity ratios in binary copolymerizations involving ES, PS and IBS have been determined from polymerization data and sequence distribution data by means of ^{13}C NMR, with results in reasonable agreement. The main characteristics of these values are:

(1) Their product, for all three copolymers examined, tends toward unity;

(2) the reactivity order, ES > PS > IBS, is in agreement with the basicity data reported [13] for the three monomers.

The small influence of the steric factor can be ascribed to the selective opening of the thiirane ring of PS and IBS between the sulphur atom and the least substituted carbon atom.

As far as the copolymer microstructure is concerned, it is necessary to distinguish between copolymers prepared at low and high conversions (only initial feed). In the first case random copolymers are obtained. In the second case, for the ES–IBS copolymers, the maximum reactivity difference between the monomers is the cause of the net prevalence of homopolymeric sequences, i.e. the accentuated deviation towards the blockiness. For the ES–PS and PS–IBS copolymers, such a deviation is quite small becoming almost negligible in the PS–IBS copolymers.

REFERENCES

1. A. Roggero, A. Mazzei, M. Bruzzone and E. Cernia, *Adv. Chem. Ser.* **142,** 330 (1975).
2. C. Corno, A. Roggero and T. Salvatori, *Europ. Polym. J.* **10** (7), 525 (1974).
3. C. Corno and A. Roggero, *Europ. Polym. J.* **12** (3), 159 (1976).
4. H. Finemann and S. D. Ross, *J. Polym. Sci.* **5** (2), 259 (1950).
5. F. P. Price, *J. chem. Phys.* **36,** 209 (1962).
6. H. J. Harwood, *A.C.S. Polymer Preprints* **8** (1), 199 (1967).
7. H. J. Harwood, *J. Polym. Sci.* **C25,** 37 (1968).
8. E. Merz, T. Alfrey and G. Goldfinger, *J. Polym. Sci.* **1,** 75 (1946).
9. W. G. Barb, *J. Polym. Sci.* **11,** 117 (1953); **18,** 310 (1955).
10. C. L. Lee, J. Smid and M. Szwarc, *Trans. Faraday Soc.* **59,** 1192 (1963).
11. D. J. Wilde and C. S. Beightler, *Foundation of Optimization.* Prentice-Hall, New Jersey (1967).
12. G. E. Ham, *Copolymerization.* p. 47, Interscience, New York (1964).
13. S. Boileau and M. F. Borsali, *C.r. hebd. Séanc. Acad. Sci., Paris* **C268,** 590 (1969).
14. (a) M. Sander, *Chem. Rev.* **66,** 297 (1966); (b) N. W. Schwartz, *J. org. Chem.* **33,** 2995 (1968).

Riassunto—Con la tecnica ^{13}C NMR è stata determinata la microstruttura con particolare riferimento alla distribuzione delle unità monomeriche nei tre copolimeri etilensolfuro–propilensolfuro (ES–PS), etilensolfuro–isobutilensolfuro (ES–IBS) e propilensolfuro–isobutilensolfuro (PS–IBS) preparati con catalizzatori di tipo anionico.

Sono stati analizzati sia copolimeri a bassa che ad alta conversione. I risultati delle frazioni di diadi e di triadi ottenuti sono stati utilizzati per il calcolo dei rapporti di reattività dei tre comonomeri.

I valori trovati in questo modo sono discussi e confrontati con quelli ottenuti col metodo classico di Finemann e Ross.