Functional terpolymers

E. ŠTAUDNER, G. KYSELÁ, A. ŽEMLIČKA, I. GOLJER, S. NOSÁLOVÁ,
and Y. SMANDROVÁ

*Department of Chemical Technology of Plastics and Fibres,
Slovak Technical University, CS-812 37 Bratislava*

Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday

In this work the terpolymerization of styrene—2-ethylhexylacrylate—maleic anhydride and α-methylstyrene—acrylonitrile—methacrylamide was studied. The composition of the terpolymer prepared at various composition of the monomer mixtures was determined by means of gas chromatography, IR and ^{13}C NMR spectroscopy. The monomer reactivity ratios of the studied ternary systems, estimated by Rosenbrock's optimization method, differ from the monomer reactivity ratios of the corresponding binary systems. The high values of the monomer reactivity ratios of some pairs indicate a great tendency to the formation of long homopolymer sequences, or sequences of the binary alternating copolymers ST—MAn, or α-MST—AN, and of acrylate homosequences 2-EHA or MeAm. The formation of longer α-MST sequences is unprobable with regard to its low upper ceiling temperature (61 °C).

The determined optimized monomer reactivity ratios for the studied ternary systems are: ST(1), MAn(2), 2-EHA(3) $r_{12} = 0.055$, $r_{21} = 0.062$, $r_{23} = 4.928$, $r_{32} = 15.188$; and α-MST(1), AN(2), MeAm(3) $r_{12} = 1.267$, $r_{21} = 0.617$, $r_{13} = 7.911$, $r_{31} = 7.231$, $r_{23} = 5.150$, $r_{32} = 16.347$.

В работе изучается терполимеризация в системах стирол—2-этил-гексилакрилат—малеиновый ангидрид и α-метилстирол—акрилонитрил—метакриламид. Состав терполимера, получаемого при различном составе смеси мономеров, определялся с помощью газовой хроматографии, а также ИК- и ^{13}C ЯМР спектроскопии. Соотношения мономерной реакционной способности изучаемых тройных систем, определенные по оптимализационному методу Розенброка, отличались от соотношений мономерной реакционной способности соответствующих бинарных систем. Высокие значения соотношений мономерной реакционной способности некоторых пар свидетельствуют о большом склоне к образованию длинных гомополимерных последовательностей или последовательностей бинарных чередующихся сополимеров ST—MAn или α-MST—AN, а также акрилатных гомо-последовательностей 2-EHA или MeAm. Образование более длинных

последовательностей α-MST маловероятно вследствие его низкой верхней предельной температуры (61 °C).

Определенные оптимизированные значения соотношений мономерной реакционной способности для изучаемых тройных систем равнялись: ST(1), MAn(2), 2-EHA(3) $r_{12} = 0.055$, $r_{21} = 0.062$, $r_{23} = 4.928$, $r_{32} = 15.188$; и α-MST(1), AN(2), MeAm(3) $r_{12} = 1.267$, $r_{21} = 0.617$, $r_{13} = 7.911$, $r_{31} = 7.231$, $r_{23} = 5.150$, $r_{32} = 16.347$.

The importance of the functional polymers lies in the possibility of the chemical transformation into special types of macromolecules. The properties of products obtained by copolymerization or terpolymerization of functional monomers with other (nonfunctional) ones can be changed in a wide range. The properties are influenced by the content and distribution of the functional monomer as well as, in the case of terpolymers, by the mutual ratio of nonfunctional monomers in the product.

The composition of terpolymers depends on values of the monomer reactivity ratios (mrr), which characterize the relative reactivity of a pair of monomers. More scientific teams, as Price and coworkers, O'Driscoll and coworkers, Tüdöss and coworkers, Hamielec and coworkers, Joshi and coworkers, and others were dealing with the mrr determination. The binary mrr do not characterize well the mutual reactivity in the ternary system, because the third monomer influences the reactivity of both other ones. For this reason, it is necessary to estimate the "optimized" monomer reactivity ratios if we want to characterize the mutual reactivity of monomers during the terpolymerization. The former can be determined by means of suitable optimization methods, whereby we start from the experimentally determined terpolymer composition and the binary monomer reactivity ratios.

In this work the terpolymerization of two monomer triplets was studied:

a) styrene—2-ethylhexylacrylate—maleic anhydride,

b) α-methylstyrene—acrylonitrile—methacrylamide.

Rosenbrock's algorithm II modified for this purpose at the Department of Chemical Technology of Plastics and Fibres was used for the determination of the optimized monomer reactivity ratios of the ternary system.

Experimental

From styrene (ST) and α-methylstyrene (α-MST), both technical grade, the stabilizer was removed by shaking with NaOH solution and distilled water and after drying with $CaCl_2$ it was vacuum-distilled in N_2 atmosphere.

From 2-ethylhexylacrylate (2-EHA) and acrylonitrile (AN), technical grade, the stabilizer was removed by a twofold vacuum distillation in N_2 atmosphere just before the polymerization.

120

Maleic anhydride (MAn), anal. grade, was used without any further purification.

Methacrylamide (MeAm) was prepared from methacrylamide sulfate by neutralization with NaOH solution. Methacrylamide was extracted by warm benzene from the mixture with Na_2SO_4. It was crystallized from benzene. M.p. = 111 °C, the purity determined by elemental analysis was 99.9 %.

The polymerization was followed gravimetrically in sealed ampoules in N_2 atmosphere. The polymers were separated by precipitation, with dried acetone or isopropanol filtration and drying to the constant mass.

The composition of ST—2-EHA—MAn was determined after polymerization by gas chromatography. In the monomer mixture the content of ST and 2-EHA was determined and from the estimated conversion the MAn content was calculated. The measuring was carried out by means of a thermal conductive gas chromatograph Carlo Erba. Conditions of measuring: temperature range 50—170 °C, programmed heating rate 5 °C min^{-1}, detector 175 °C, injector 150 °C, feedstock 10 mm^3, flow rate of air and helium 52 cm^3 min^{-1}, solvent acetone, standard butyl acetate. The composition of α-MST—AN—MeAm terpolymers was determined by IR spectroscopy from the ratio of the absorbance bands $\tilde{v}(C \equiv N)$ (2242 cm^{-1}), $\tilde{v}(C = O)$ (1660 cm^{-1}) and from the C—H bending vibrations of the aromatic ring $\tilde{v}(C—H)$ (758 cm^{-1}). The samples were measured by means of KBr technique on the device MOM 2000. Both terpolymers were also analyzed by ^{13}C NMR spectroscopy. The measuring was carried out on the NMR spectrometer FX-100 Jeol at the Chemical Faculty of the Slovak Technical University. The working frequency was 25.047 MHz, the induction of the magnetic field 2.3 T, the spectral range 6000 MHz, the number of detected points 8192, the number of accumulations 5000. SiO_2 cells with 10 mm outside diameter were used. The concentration of polymers was 10 mass %, the measuring temperature 50 °C, the solvent deutero-acetone. The integral curves were evaluated.

Results and discussion

Terpolymers of styrene—2-ethylhexylacrylate—maleic anhydride were prepared by mass polymerization in ampoules at 70 °C in nitrogen atmosphere at constant initiator concentration (dibenzoyl peroxide) — 0.1 mass % relating to the monomer mixture. They were separated by precipitation with dried isopropanol.

Terpolymers of α-methylstyrene—acrylonitrile—methacrylamide were prepared by terpolymerization in solution of dried acetone. The total monomer concentration was constant (34.53 mass % relating to the mixture). The dibenzoyl peroxide concentration was 0.5 mass % relating to the mixture and the polymerization temperature was 70 °C. The terpolymers were separated by precipitation with methanol.

In Tables 1 and 2 are the conditions for the preparation of both terpolymer types and there is the composition determined by gas chromatography and

E. ŠTAUDNER, G. KYSELÁ, A. ŽEMLIČKA, I. GOLJER, S. NOSÁLOVÁ, Y SMANDROVÁ

Table 1

Terpolymerization conditions for ST—2-EHA—MAn and composition of the terpolymers
Temperature 70 °C (Series *A*)

Sample	Polymerization time	Conversion	Monomer charge			Terpolymer		
	min	%	x_{ST}	x_{MAn}	x_{2-EHA}	y_{ST}	y_{MAn}	y_{2-EHA}
A-I	8	13.0	0.05	0.05	0.90	0.188	0.097	0.715
A-II	9	8.2	0.10	0.10	0.80	0.354	0.258	0.388
A-III	11	17.3	0.15	0.15	0.70	0.363	0.283	0.354
A-IV	11	55.2	0.20	0.20	0.60	0.275	0.219	0.506
A-V	11	55.9	0.25	0.25	0.50	0.339	0.281	0.381

Table 2

Terpolymerization conditions for α-MST—AN—MeAm and composition of the terpolymers
Temperature 70 °C (Series *B*)

Sample	Polymerization time	Conversion	Monomer charge			Terpolymer		
	min	%	$x_{\alpha-MST}$	x_{AN}	x_{MeAm}	$y_{\alpha-MST}$	y_{AN}	y_{MeAm}
B-I	150	7.27	0.1	0.8	0.1	0.242	0.670	0.088
B-II	350	5.82	0.5	0.4	0.1	0.576	0.387	0.037
B-III	250	6.54	0.3	0.4	0.3	0.385	0.514	0.101
B-IV	220	9.10	0.3	0.6	0.1	0.429	0.524	0.047

^{13}C NMR spectroscopy (Table 1, Series *A*) or by IR and ^{13}C NMR spectroscopy (Table 2, Series *B*). The composition of the monomer charges is quoted in mole fractions of monomers *x* and the composition of terpolymers in mole fractions *y* (the symbols are in agreement with those used in the literature, *e.g.* [1]).

The evaluation of the results was carried out with the computer EC 1010 of the Computer Centre of the Chemical Faculty of the Slovak Technical University. Rosenbrock's algorithm II [2] for the solution of problems with limitation for the calculation of the extreme of the objective function (OF) was used for the "optimization" of the monomer reactivity ratios of the ternary system. This method belongs to the methods of direct search of the minimum of the designed function and has an iterative character. The calculation of the optimum values of the monomer reactivity ratios was carried out by subsequent approximation from the initial values (monomer reactivity ratios of binary systems from the literature or determined ones) to the values, when the condition for the completion of the calculation (suggestion) is fulfilled

122

$$OF(k + 1) - OF(k) = \varepsilon$$

ε is the suggested maximum difference of the $k + 1$ and the k iteration of the designed function, in our case $\varepsilon = 10^{-3}$

Table 3

Comparison of binary [3] and optimized monomer reactivity ratios (for the ternary system) for terpolymers ST—2-EHA—MAn

1st Monomer	2nd Monomer	r_{12}		r_{21}	
		Optimized	Ref. [3]	Optimized	Ref. [3]
ST	MAn	0.055	0.020	0.062	0.001
ST	2-EHA	0.705	0.940	1.658	0.260
MAn	2-EHA	4.928	0.009[a]	15.188	3.682[a]

a) Calculated from the Q—e values.

Table 4

Comparison of binary [3] and optimized monomer reactivity ratios (for the ternary system) for terpolymers α-MST—AN—MeAm

1st Monomer	2nd Monomer	r_{12}		r_{21}	
		Optimized	Ref. [3]	Optimized	Ref. [3]
α-MST	AN	1.267	0.24	0.617	0.045
α-MST	MeAm	7.911	0.128[a]	7.231	0.117[a]
AN	MeAm	5.150	0.028[a]	16.347	2.874[a]

a) Calculated from the Q—e values.

The form of the designed function is

$$OF = \sum_{i=1}^{n} |LS_i - RS_i| = \text{minimum}$$

LS_i and RS_i is the left and the right side of the rearranged copolymerization equation for terpolymerization [1], n is the number of experimental data.

$$LS_i = y_{1i} \cdot x_{2i} \left[\frac{x_{1i}}{r(k)_{12} \cdot r(k)_{21}} + \frac{x_{2i}}{r(k)_{12} \cdot r(k)_{32}} + \frac{x_{3i}}{r(k)_{32} \cdot r(k)_{13}} \right] \cdot$$
$$\cdot \left[x_{2i} + \frac{x_{1i}}{r(k)_{21}} + \frac{x_{3i}}{r(k)_{23}} \right]$$

$$RS_i = y_{2i} \cdot x_{1i} \left[\frac{x_{1i}}{r(k)_{31} \cdot r(k)_{21}} + \frac{x_{2i}}{r(k)_{21} \cdot r(k)_{32}} + \frac{x_{3i}}{r(k)_{31} \cdot r(k)_{23}} \right] \cdot$$

$$\cdot \left[x_{1i} + \frac{x_{2i}}{r(k)_{12}} + \frac{x_{3i}}{r(k)_{13}} \right]$$

x_1, x_2, x_3 are mole fractions of monomers in the monomer charge, y_1, y_2, y_3 are mole fractions of monomers in terpolymer.

The results of the optimization of the monomer reactivity ratios are summarized in Tables 3 and 4. The high values of the monomer reactivity ratios of some pairs indicate a high tendency to the formation of long homopolymer sequences [4] in the studied terpolymerization systems, or sequences of the binary alternating copolymers ST—MAn, or α-MST—AN, and of acrylate homosequences 2-EHA or MeAm. The formation of longer α-MST sequences is unprobable with regard to its low upper ceiling temperature (61 °C).

References

1. Kučera, M., *Mechanismus a kinetika polymerací.* (Mechanism and Kinetics of Polymerization.) Academia, Prague, 1984.
2. Kuster, J. L. and Mize, J. H., *Optimization Techniques with Fortran,* pp. 385—398. McGraw-Hill, New York, 1975.
3. Brandrup, J. and Immergut, E. H., *Polymer Handbook.* Wiley, London, 1975.
4. Sawada, H., *Thermodynamics of Polymerization.* M. Dekker, New York, 1976.

Translated by P. Rosner