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Multicomponent Copolymerization on Display

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SUMMARY: Potentialities of the employment of the software modeling tool "Copolymerization for Windows" developed by us for the calculation of statistical characteristics of chemical structure of multicomponent copolymers as well as for the prediction of their transparency and thermostability are exemplified by terpolymerization of styrene, methyl methacrylate and acrylonitrile.

Today polymer science disposes of well-elaborate theory of free-radical copolymerization of an arbitrary number of monomers *m,* enabling one to determine many statistical characteristics of chemical structure of copolymers as well as to predict their important service properties $^{1)}$. However, the use of this theory in practice for the description of particular systems until recently was mainly restricted to the case $m = 2$. Only in this simplest case basic equations of the copolymerization

$$(1-p)\frac{dx_\alpha}{dp} = x_\alpha - X_\alpha(\mathbf{x}),\ x_\alpha(0) = x_\alpha^0\ (\alpha = 1,\dots,m) \tag{1}$$

describing the drift of a monomer mixture composition $\mathbf{x}(p)$ with overall conversion of monomers p have analytical solution. The dependence of the components X_α of the vector of an instant copolymer composition $\mathbf{X}$ on $\mathbf{x}$ is markedly nonlinear $^{1)}$. This circumstance conditions the possibility of the existence of more than one stable stationary solution of the set of equations (1). In accordance with the number of such attractors $(m-1)$-dimensional phase space $x_1 + \cdots + x_m = 1$ (*m*-simplex) of the set (1) is divided into basins of attraction of each attractor, separated by the separatrix manifolds of the dimension $(m-2)$. Such a structure of a simplex provides the explanation of experimentally observed situation when two copolymer specimens of nearly identical composition were found to substantially differ in their performance properties. This situation takes place under conversion p close to 1 provided the initial points of trajectories of dynamic system (1), characterizing the evolution of $\mathbf{x}(p)$ in the course of the synthesis of these two specimens, being close to one another in the simplex

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fall, however, within the basins of distinct attractors (see Fig. 1). The last circumstance is responsible for qualitatively different character of the trajectories $\mathbf{x}(p)$ and, consequently, for the properties of a copolymer formed.

Table 1. Input parameters which are necessary to specify in order for the calculations to be performed by the program CW and output data to be obtained.

Input information	***Output Information***
Number of monomers	Composition of monomer mixture $\mathbf{x}$
Reactivity ratios $\{r_{\alpha\beta}\}$	Instantaneous copolymer composition $\mathbf{X}$
Initial stoichiometry $\mathbf{x}^0$	Average composition of copolymer $\langle \mathbf{X} \rangle$
	Averaged fractions of dyads, triads, tetrads and pentads
	Composition distribution
	Stationary points $\mathbf{x}^*$
Glass transition temperatures of homopolymers $T_{\alpha\alpha}$ and alternating binary copolymers $T_{\alpha\beta}\,(\alpha \neq \beta)$	Glass transition temperature T_g
Flory-Huggins parameters $\{\chi_{\alpha\beta}\}$	Enthalpy of mixing ΔH
Interaction energy densities $\{B_{\alpha\beta}\}$	

To ensure the possibility to employ the results of modern quantitative theory of copolymerization 1) for the calculation of statistical characteristics of multicomponent copolymers, as well as for the prediction of such important properties as the transparency and thermostability, we developed computer program "Copolymerization for Windows" (CW) 2) (See Table 1). This program permits the calculation of the copolymerization of up to six monomers. In order to illustrate its potentialities below there will be presented the results of the calculation of copolymerization of three monomers M_1 (Styrene) + M_2 (Methyl methacrylate) + M_3 (Acrylonitrile). As well as being of considerable commercial value this copolymer is particularly suitable for the illustration of CW capabilities because a complete set of the input parameters (2), (3) for the process of its synthesis necessary for the calculation by means of CW is available in literature 3-7).

$$\{r_{\alpha\beta}\} = \begin{pmatrix} 1 & 0.52 & 0.37 \\ 0.46 & 1 & 1.20 \\ 0.05 & 0.15 & 1 \end{pmatrix} \tag{2}$$

$$\{T_{\alpha\beta}\} = \begin{pmatrix} 95 & 91 & 112 \\ 91 & 99 & 79 \\ 112 & 79 & 105 \end{pmatrix}, (°C),\quad \{B_{\alpha\beta}\} = \begin{pmatrix} 0 & 0.71 & 22.80 \\ 0.71 & 0 & 11.30 \\ 22.80 & 11.30 & 0 \end{pmatrix}, (J/cm^3) \tag{3}$$

The program incorporates two regimes of performing the calculations. In the first of them provision is made for fixing all input parameters and finding the dependencies on conversion p of all statistical characteristics of a copolymer and thus of all its service properties. Conversely, in the second regime fixed is the conversion and the values of these parameters are supposed to be calculated within the whole range of initial compositions $\mathbf{x}^0$. Among the Figures presented below, Fig. 1, 3 and 4 apply to the regime I, while the rest of them, 2 and 5, refer to the regime II.

As it follows from Fig. 1 the Gibbs triangle for terpolymerization (ST + MMA + AN) is divided by the separatrix into two basins of attraction of two attractors. Fig. 2 demonstrates that within the first of these basins, corresponding to the attractor in the left apex of the triangle, the values of the heat of mixing turn out to be appreciably less than those of the basin of attraction of other attractor located in the upper apex of the triangle. This is indicative of the fact that enriching of terpolymers with Styrene favors their compatibility.

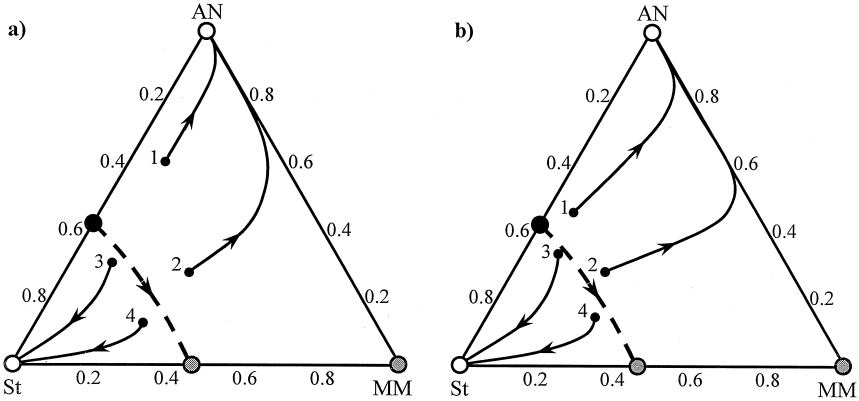


Fig. 1. Conversion drift of monomer mixture composition (a) and a copolymer instantaneous composition (b) under its different initial values (0.3, 0.1, 0.6) (1); (0.4, 0.3, 0.3) (2); (0.6, 0.1, 0.3) (3); (0.6, 0.3, 0.1) (4). Stationary points are depicted by big circles. Open, black filled and gray filled circles correspond to attractors, repellers and saddles, respectively. Dashed heavy line represents the separatrix.

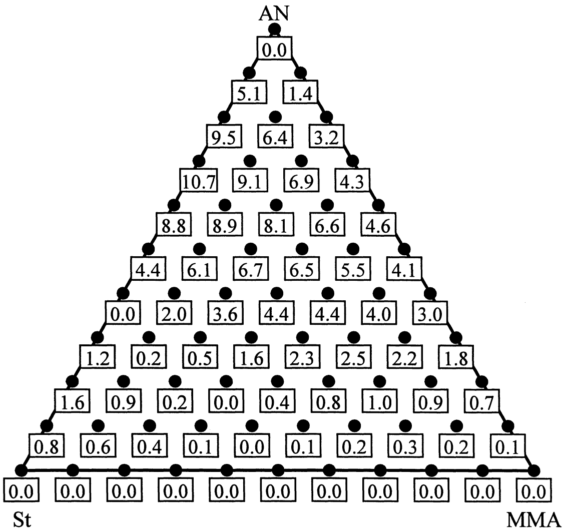


Fig. 2. Values of the heat of mixing $\Delta H \cdot 10$ (J/cm^3) for terpolymers (ST + MMA + AN) of different composition obtained under complete conversion of monomers. This conditions the loss of a system transparency due to phase separation can be prognosticated in the course of the terpolymerization.

Composition inhomogeneity of the copolymerization products prepared at high conversions may be responsible for their phase separation and, thus, for the loss of the transparency resulting in the deterioration of some performance properties. That is why the task of calculation of the evolution of the composition distribution (or its one-dimensional sections) with conversion is one of the hottest. The character of this evolution is prescribed by the initial monomer mixture composition as it is clearly demonstrated on Fig. 3 and 4. On the first of them all one-dimensional sections remain unimodal up to complete conversion of the monomers, which testifies to reasonable compatibility of the copolymerization products. A different situation is observed on Fig. 4, where with the growth of conversion the appearance may be expected of the second and even the third mode of the distributions $f_\alpha(\zeta_\alpha)$. Under these conditions the loss of a system transparency due to phase separation can be prognosticated in the course of the terpolymerization.

On Fig. 5 the results are reported of the calculation of T_g under the regime II. For the particular system chosen the distinction in glass transition temperature of terpolymers of different composition proves to be negligible. However, there is plenty of other systems of crucial practical importance where these distinctions may be very substantial.

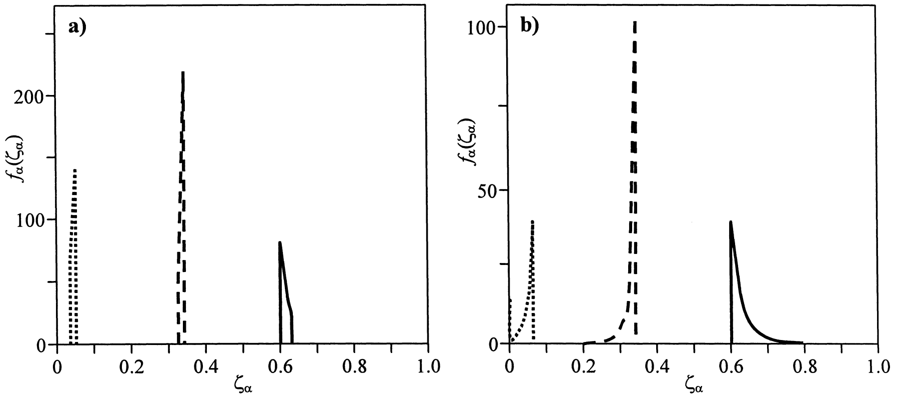


Fig. 3. Distribution of macromolecules $f_\alpha(\zeta_\alpha)$ ($\alpha = 1, 2, 3$) for fractions in them of ζ_α monomeric units $\overline{\mathrm{M}}_\alpha$ at initial monomer mixture composition (0.64, 0.32, 0.04) for the values of conversion p equal to 0.5 (a) and 1 (b). Solid, dashed and dotted lines correspond to monomeric units of type $\alpha = 1$, 2 and 3 respectively.

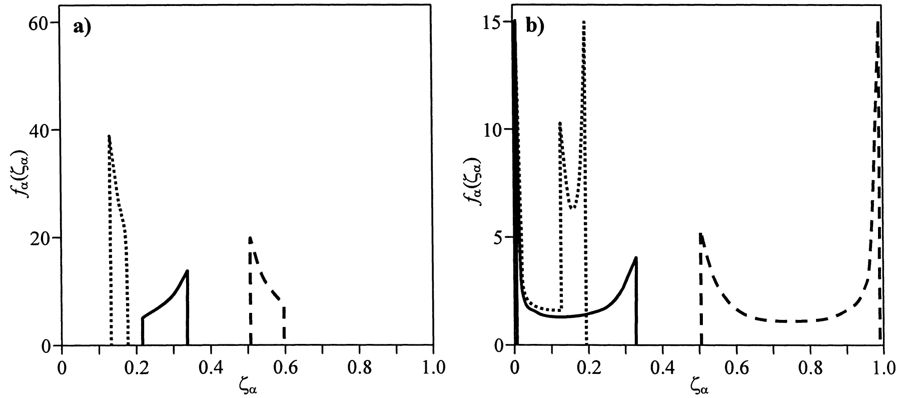
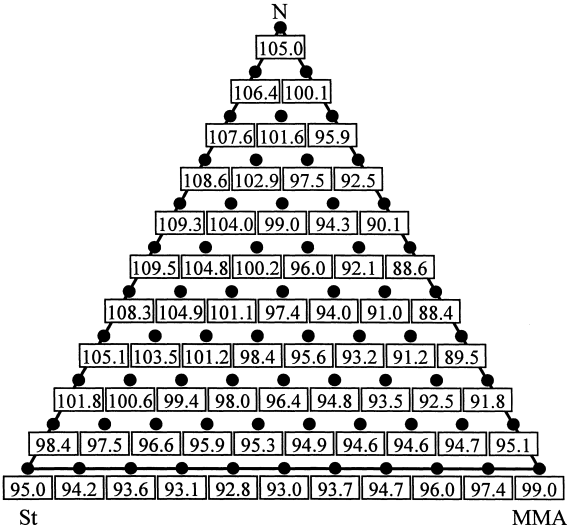


Fig. 4. One-dimensional sections of composition distribution identical to those depicted on Fig. 3, but at initial monomer mixture composition (0.1, 0.1, 0.8) for the values of conversion p equal to 0.25 (a) and 1 (b).

To our viewpoint the computer program CW may be taken up as an instrument for mathematical modeling of many actual processes of multicomponent copolymerization. This assertion stems from the fact that on the one hand this program is based on physicochemically grounded kinetic models, while on the other hand these models' parameters may be readily found in literature for a number of systems of practical significance.



N

105.0

106.4 100.1

107.6 101.6 95.9

108.6 102.9 97.5 92.5

109.3 104.0 99.0 94.3 90.1

109.5 104.8 100.2 96.0 92.1 88.6

108.3 104.9 101.1 97.4 94.0 91.0 88.4

105.1 103.5 101.2 98.4 95.6 93.2 91.2 89.5

101.8 100.6 99.4 98.0 96.4 94.8 93.5 92.5 91.8

98.4 97.5 96.6 95.9 95.3 94.9 94.6 94.6 94.7 95.1

95.0 94.2 93.6 93.1 92.8 93.0 93.7 94.7 96.0 97.4 99.0

St MMA

Fig. 5. Glass transition temperature T_g (°C) of the products of terpolymerization (ST + MMA + AN) obtained at conversion $p = 1$.

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