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Determination of the Monomer Donor-Acceptor Complexes Participation in the Alternating Propagating Reaction Based on the Microtacticity of the Alternating Copolymers

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SUMMARY

It is shown that the probability for the formation of alternating macromolecules by monomer donor- acceptor complexes can be determined from the microtacticity of the copolymers. If the stereoregularity in the alternating copolymerization is described by the Bernoullian trial two other probabilities concerning the meso-diad formation can be determined by this method. If the stereoregularity is described by the first order Markov chain the transition probabilities can be calculated. Thus a more detailed analysis of the propagation mechanism in alternating copolymerization can be carried out.

Recently the kinetic methods for the determination of the probability (α) of the alternating macromolecules formation by monomer donor- acceptor complexes were proposed (GEORGIEV, GOLUBEV, ZUBOV 1978). The value of α provides a fundamental information about the mechanism of the alternating copolymerization. In this work it is shown that α can also be determined from the microtacticity of the alternating copolymers.

If the stereoregularity in the alternating copolymerization is described by the Bernoullian trial, it is necessary to introduce at least two other probabilities:

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γ - the probability of the meso-diad formation between the last two monomeric units of the propagation chain in the addition of the free monomer or donor- acceptor complexes to this chain, and β - the probability of the meso-diad formation between the last monomeric unit of the propagation chain and one of the adding donor- acceptor´s components. Then it is easy to find that the mole fraction of the meso-diad (m) in the alternating macromolecules is $m = (\gamma + \beta)/(1 + \alpha)$. The concentration of the donor- acceptor complexes can be affected by changes of the monomer concentration. Therefore the probability α can vary too. Hence, the following system of equations is obtained: $m_i = \gamma + \alpha_i(\beta - m_i)$ $(i = 1,2,3)$. By solving this system, the probability α is obtained: $\alpha = (m_1 - m_2)/[\nu_2 m_2 - m_1 + \beta(1 - \nu_2)]$

where $\beta = [(m_1 - m_2)(\nu_3 m_3 - m_1) - (m_1 - m_3)(\nu_2 m_2 - m_1)] /[(m_1 - m_3)(1 - \nu_2) - (m_1 - m_2)(1 - \nu_3)]$,

$\nu_1 = \alpha_1/\alpha_2$ and $\nu_2 = \alpha_1/\alpha_3$. The parameters ν_1 and ν_2 are determined experimentally by controlled variation of the monomer concentration.

If the stereoregularity in the alternating copolymerization is described by the first order Markov chain, the following transition probabilities are introduced: $P^{r}_{m\to m}$ and $P^{r}_{m\to r}$, $P^{r}_{r\to m}$ and $P^{r}_{r\to r}$, $P^{a}_{m\to m}$ and $P^{a}_{m\to r}$, $P^{a}_{r\to m}$ and $P^{a}_{r\to r}$. The upper index (r or a) shows that the formation of a diad involves the last two monomeric units of the propagation chain or the last monomeric unit of this chain and one of the complex component. The sum of the probabilities in every pair is equal to one. Hence the number of the unknown probabilities is four. It is easy to determine the transition probabilities from one type diad to another one. They form a nonstochastic positive definite matrix. After its transformation (GANTMACHER 1959) the transition matrix (P) of the considered Markov chain is obtained:

$$P = \begin{array}{c|cc} & m & r \\ \hline m & \dfrac{P^r_{m\to m} + \alpha P^a_{m\to m}}{1+\alpha} & \dfrac{P^r_{m\to r} + \alpha P^a_{m\to r}}{1+\alpha} \\ r & \dfrac{P^r_{r\to m} + \alpha P^a_{r\to m}}{1+\alpha} & \dfrac{P^r_{r\to r} + \alpha P^a_{r\to r}}{1+\alpha} \end{array}$$

The components of the eigenvektor of this matrix are equal to the mole fraction of the meso (m) and racemic (r) diads in macromolecules:

$$m = A^{-1}\left[P^a_{r\to m} + P^a_{r\to m} + (P^a_{r\to m} + P^a_{m\to r})\right] \qquad \text{where}$$

$A = P^r_{r\to m} + P^r_{m\to r}$. In this case the system of equations is also obtained by the variation of α . The parameters $P^r_{r\to m}/A$, $P^a_{r\to m}/A$, $(P^a_{r\to m} + P^a_{m\to r})/A$ and α are determined by numerical solution of this system. Analytical expression for α can be obtained if the derivative $dm/d\alpha = B$ is determined. Then $\alpha = (D - CE)/B(1 + C)^2$ where:

$$C = \begin{vmatrix} 1-\nu_2 & m_1 - m_2 \\ 1-\nu_3 & m_1 - m_3 \end{vmatrix} : \begin{vmatrix} 1-\nu_2 & m_1 - \nu_2 m_2 \\ 1-\nu_3 & m_1 - \nu_3 m_3 \end{vmatrix}$$

$$D = \begin{vmatrix} m_1 - m_2 & m_1 - \nu_2 m_2 \\ m_1 - m_3 & m_1 - \nu_3 m_3 \end{vmatrix} : \begin{vmatrix} 1-\nu_2 & m_1 - \nu_2 m_2 \\ 1-\nu_3 & m_1 - \nu_3 m_3 \end{vmatrix} \qquad \text{and}$$

$$E = m_i - D + m_i C \quad (i = 1,2,3) \ .$$

Besides α the probabilities β and γ (in stereoregularity by Bernoullian trial) and the above mentioned transition probabilities (in stereoregularity by the first order Markov chain) can be determined by this method. These results allow to carry out a more detailed analysis of the propagating mechanism in alternating copolymerization.

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