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Determination of the Participation of Donor-Acceptor Complexes in Copolymerizations from NMR Data

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SUMMARY

A new method is developed which enables a quantitative estimation of the participation of donor-acceptor complexes in copolymerizations from the triad copolymer composition. Rate constant ratios may be calculated by this method as well, allowing to evaluate the effect of the complex formation on the monomer reactivities.

INTRODUCTION

In the recent decade many data, showing the participation of monomer donor-acceptor complexes (DAC) in copolymerizations have been obtained (BUTLER and CAMPUS 1970, FURT and RHODES 1974, GAYLORD and PATNAIK 1975). The quantitative estimation of their participation is essential for a correct determination of the monomer reactivities and for an explanation of the experimental deviations from the copolymer composition equation. In some methods which are elaborated for this aim, the special copolymerization processes are discussed (SHIROTA et al. 1974, GEORGIEV and ZUBOV 1978, GEORGIEV and ZUBOV 1979). In others (SEINER and LITT 1971, LITT 1971, KUCHER et al. 1978) the values of the complex formation constant (K) and of the rate constants are calculated by a proper computer procedure in such a way, that the theoretical and experimental dependences of the copolymer compositions and the copolymerization rates are in close agreement. No method is existing, however, which allows to check the participation of DAC in a copolymerization, to determine the degree of this participation in the propagation reaction and to calculate the characteristic parameters for the monomers and DAC reactivities from NMR study.

RESULTS AND DISCUSSION

When DAC between the monomers A and B (AB) takes part in the copolymerization, the kinetic scheme will be as follows:

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$$\sim A^{\cdot} + A \xrightarrow{k_{AA}} \sim A^{\cdot} \quad (1) \qquad \sim A^{\cdot} + AB \xrightarrow{k_{AAB}} \sim B^{\cdot} \quad (5)$$

$$\sim A^{\cdot} + B \xrightarrow{k_{AB}} \sim B^{\cdot} \quad (2) \qquad \sim A^{\cdot} + BA \xrightarrow{k_{ABA}} \sim A^{\cdot} \quad (6)$$

$$\sim B^{\cdot} + A \xrightarrow{k_{BA}} \sim A^{\cdot} \quad (3) \qquad \sim B^{\cdot} + BA \xrightarrow{k_{BBA}} \sim A^{\cdot} \quad (7)$$

$$\sim B^{\cdot} + B \xrightarrow{k_{BB}} \sim B^{\cdot} \quad (4) \qquad \sim B^{\cdot} + AB \xrightarrow{k_{BAB}} \sim B^{\cdot} \quad (8)$$

The addition of AB to the propagating end can be splitted conventionally into two steps. The first component of AB is involved in the polymer chain at first, forming a new active end which reacts only with the other part of AB in the second step of the AB-addition. In this way two types of chains of differing reactivity are defined, two of the type A ($\sim A^{\cdot}$ and $\sim A^{\cdot *}$) and two active chaines of the type B ($\sim B^{\cdot}$ and $\sim B^{\cdot *}$). The chains $\sim A^{\cdot *}$ and $\sim B^{\cdot *}$ are formed after the first step of the AB-addition only. Thus, the problem for the determination of the probability for the formation of the copolymer molecules by a AB-addition (P(C)) is reduced to the estimation of the average times of occurrence in the conditions $A^{\cdot *}$ (F^{*}_{A}) and $B^{\cdot *}$ (F^{*}_{B}).

$$P(C) = 2(F^{*}_{A} + F^{*}_{B}) \qquad (9)$$

The problem may be solved if the propagation reaction is sumulated by the Markov's chain with four states (A, A^{*}, B and B^{*}). As the values of K are much less than unity usually, [AB] = K [A][B]. Then the components of the transition matrix (P) of this Markov's chain

$$P = \begin{array}{c|cccc} & A & A^{*} & B & B^{*} \\ \hline A & p_{AA} & p^{*}_{AA} & p_{AB} & p^{*}_{AB} \\ A^{*} & 0 & 0 & 1 & 0 \\ B & p_{BA} & p^{*}_{BA} & p_{BB} & p^{*}_{BB} \\ B^{*} & 1 & 0 & 0 & 0 \end{array} \qquad (10)$$

are represented by the concentrations [A], [B] and by the six ratios of the rate constants ($q_1=k_{AA}/k_{AB}$, $q_2=k_{BB}/k_{BA}$, $f_1=k_{AA}/k_{AAA}$, $f_2=k_{AB}/k_{ABA}$, $f_3=k_{BB}/k_{BBA}$, $f_4=k_{BA}/k_{BAB}$) by the following way:

$$p_{AA} = q_1[A]/\mu_1 \quad (11) \qquad p^{*}_{AA} = Kq_1f_1[A][B]/\mu_1 \quad (12)$$

$$p_{AB} = [B]/\mu_1 \quad (13) \qquad p^{*}_{AB} = Kf_2[A][B]/\mu_1 \quad (14)$$

$$p_{BB} = q_2[B]/\mu_2 \quad (15) \qquad p^{*}_{BB} = Kq_2f_3[A][B]/\mu_2 \quad (16)$$

$$p_{BA} = [A]/\mu_2 \quad (17) \qquad p^{*}_{BA} = Kf_4[A][B]/\mu_2 \quad (18)$$

In the above equations $\mu_1 = q_1[A](1+Kf_1[B]) + (Kf_2[A]+1)[B]$

and $\mathcal{M}_2 = q_2[B](1 + Kf_3[A]) + (1 + Kf_4[B])[A]$. The average time of occurance of the propagating chain in the states A, A^{*}, B and B^{*} can be determined from the relation $\bar{\bar{F}}P = \bar{F}$ ($\bar{\bar{F}} = (F_A, F_A^{*}, F_B, F_B^{*})$) (PRICE 1962):

$$F_A = (m_B p_{BA}^{*} - m_A(1 - p_{BA}))/\mathcal{M}_3 \tag{19}$$

$$F_A^{*} = (p_{BA}^{*} ((1 - p_{AA})m_A - m_B) - m_A p_{AA}^{*}(1 - p_{BA}))/\mathcal{M}_3 \tag{20}$$

$$F_B = (m_A(1 - p_{AA}) - m_B(1 + p_{AA}^{*}))/\mathcal{M}_3 \tag{21}$$

$$F_B^{*} = ((m_B p_{BA}^{*} - m_A)(1 - p_{AA}) + m_B p_{BA}(1 + p_{AA}^{*}))/\mathcal{M}_3 \tag{22}$$

where m_A and m_B are the mole fractions of the units A and B in the copolymer molecules and $\mathcal{M}_3 = p_{BA}^{*} (1 - p_{AA})-(1-p_{BA})(1+p_{AA}^{*})$.

The decomposition of the AB-addition results in the number of the ending diads and triads which become two times higher as before. The average times of occurrence of the propagating chains in these states are expressed by the elements of the matrix P and by F_A, F_A^{*}, F_B and F_B^{*} (as determined above):

$F_{AA} = F_A p_{AA}$, $F_{AB} = F_A p_{AB} + F_A^{*}$, $F_{BA} = F_B p_{BA} + F_B^{*}$, $F_{BB}=F_B p_{BB}$,

$F_{AA}^{*} = F_A p_{AA}^{*}$, $F_{AB}^{*} = F_A p_{AB}^{*}$, $F_{BA}^{*} = F_B p_{BA}^{*}$, $F_{BB}^{*} = F_B p_{BB}^{*}$,

$F_{AAA} = F_A p_{AA} p_{AA}$, $F_{AAB} = F_A p_{AA} p_{AB} + F_A p_{AA}^{*}$,

$F_{ABA} = F_A p_{AB} p_{BA} + F_A p_{AB}^{*} + F_A^{*} p_{BA}$, $F_{ABB} = F_A p_{AB} p_{BB} + F_A^{*} p_{BB}$,

$F_{BAA} = F_B p_{BA} p_{AA} + F_B^{*} p_{AA}$, $F_{BAB} = F_B p_{BA} p_{AB} + F_B^{*} p_{AB} + F_B p_{BA}^{*}$,

$F_{BBA} = F_B p_{BB} p_{BA} + F_B p_{BB}^{*}$, $F_{BBB} = F_B p_{BB} p_{BB}$, $F_{AAA}^{*} = F_A p_{AA} p_{AA}^{*}$,

$F_{AAB}^{*} = F_A p_{AA} p_{AB}^{*}$, $F_{ABA}^{*} = F_A p_{AB} p_{BA}^{*} + F_A^{*} p_{BA}^{*}$,

$F_{ABB}^{*} = F_A p_{AB} p_{BB}^{*} + F_A^{*} p_{BB}^{*}$, $F_{BAA}^{*} = F_B p_{BA} p_{AA}^{*} + F_B^{*} p_{AA}^{*}$,

$F_{BAB}^{*} = F_B p_{BA} p_{AB}^{*} + F_B^{*} p_{AB}^{*}$, $F_{BBA}^{*} = F_B p_{BB} p_{BA}^{*}$, $F_{BBB}^{*} = F_B p_{BB} p_{BB}^{*}$.

The mole fractions of the following diads and triads can be determined by NMR-spectroscopy:

$$m_{AA} = F_{AA} + F_{AA}^{*} = F_A(p_{AA} + p_{AA}^{*}) \tag{23}$$

$$m_{BB} = F_{BB} + F_{BB}^{*} = F_B(p_{BB} + p_{BB}^{*}) \tag{24}$$

$$m_{AB} + m_{BA} = F_{AB} + F_{AB}^{*} + F_{BA} + F_{BA}^{*} = 1 - m_{AA} - m_{BB} \tag{25}$$

$$m_{AAA} = F_{AAA} + F_{AAA}^{*} = F_A p_{AA}(p_{AA} + p_{AA}^{*}) \tag{26}$$

$$\begin{aligned} m_{AAB} + m_{BAA} &= F_{AAB} + F_{AAB}^{*} + F_{BAA} + F_{BAA}^{*} \\ &= (F_A (1 - p_{AA}) + F_B p_{BA} + F_B^{*})(p_{AA} + p_{AA}^{*}) \end{aligned} \tag{27}$$

$$m_{ABB} + m_{BBA} = F_{ABB} + F^{*}_{ABB} + F_{BBA} + F^{*}_{BBA}$$

$$= (F_B(1-p_{BB}) + F^{*}_{A} + F_A p_{AB})(p_{BB} + p^{*}_{BB}) \qquad (28)$$

$$m_{BBB} = F_{BBB} + F^{*}_{BBB} = F_B p_{BB}(p_{BB} + p^{*}_{BB}) \qquad (29)$$

$$m_{ABA} = F_{ABA} + F^{*}_{ABA} = m_A - ((F_A p_{AB} + F^{*}_{A})(p_{BB} + p^{*}_{BB}) + F_A(p_{AA} + p^{*}_{AA})) \qquad (30)$$

$$m_{BAB} = F_{BAB} + F^{*}_{BAB} = m_B - ((F_B p_{BA} + F^{*}_{B})(p_{AA} + p^{*}_{AA}) + F_B(p_{BB} + p^{*}_{BB})) \qquad (31)$$

From the eqs. (22) and (25) it follows that

$$p_{AA} = m_{AAA}/m_{AA} \qquad (32)$$

and from eqs (23) and (28)

$$p_{BB} = m_{BBB}/m_{BB} \qquad (33)$$

It is obvious from eqs. (11) and (15) that both the probabilities and the experimentally determined ratios m_{AAA}/m_{AA} and m_{BBB}/m_{BB} depend on the concentration [AB], if AB takes part in the propagation reaction. These dependences allow the AB-participation in the propagation reaction to prove a posteriori. For this purpose it is necessary to check the effect of the total monomer concentration ([M] =[A] + [B]) on the ratios m_{AAA}/m_{AA} and m_{BBB}/m_{BB} at constant [A]/[B]. Such an effect allows to determine the probabilities p_{AB} and p_{BA} also. For this purpose the linearization of the eqs. (11) and (15) is used:

$$[A]^{-1} = -K(q_1 f_1 + f_2) + q_1(m_{AAA} - m_{AA})([B]\, m_{AAA})^{-1} \qquad (34)$$

$$[B]^{-1} = -K(q_2 f_3 + f_4) + q_2(m_{BBB} - m_{BB})([A]\, m_{BBB})^{-1} \qquad (35)$$

From the eqs. (13) and (17) it is seen that the values of p_{AB} p_{BA} can be calculated from the intercepts and slopes of these lines. In such a way the probability sums $p^{*}_{AA} + p^{*}_{AB} = 1 - p_{AA} - p_{BA}$ can be calculated too.

The expressions for the mole fractions m_{ABA} (30) and m_{BAB} (31) can be used for the determination of the probabilities p^{*}_{AA} and p^{*}_{BB}. The following system is obtained after a substitution of the expressions for F_A (19), F_B (21), F^{*}_{A} (20) and F^{*}_{B} (22) in eqs. (30) and (31):

$$\left| \begin{array}{l} Qp^{*}_{AA} + Rp^{*}_{BA} = S \\ -Tp^{*}_{AA} + Up^{*}_{BA} = V \end{array} \right. \qquad (36)$$

where $Q = m_A(1 - p_{BA}) - L$, $R = m_B(1 - p_{AB}) - m_A(1 - p_{AA})$,
$S = m_A(p_{BA} - 1)p_{AB} + L(m_B - m_A(1 - p_{AA}))$, $T = p_{BA}(1 + m_B)$,
$U = (M + p_{AA} - 1)m_B$, $V = m_A(p_{BA} - 1)(1 - p_{AA} - M)$,
$L = (m_A + m_{AA} - m_{AAA})/m_{BB}$ and $M = (m_B + m_{BB} - m_{BBB})/m_{AA}$.
Then $p^*_{AA} = (SU - RV)/\mathcal{M}_6$, $p^*_{BA} = (QV - ST)/\mathcal{M}_6$,
$p^*_{AB} = 1 - p_{AA} - p_{AB} - p^*_{AA}$ and $p^*_{BB} = 1 - p_{BB} - p_{BA} - p^*_{BA}$
where $\mathcal{M}_6 = QU + TR$.

Another method for the determination of p^*_{AA} and p^*_{BA} is based on a linearization of the systems eqs. (36) after substitutions of the expressions for p^*_{AA} (12) and p^*_{BA} (18) within.

$$S\mathcal{M}_1(q_1Q\,[A][B])^{-1} = Kf_1 + R\mathcal{M}_1(q_1\mathcal{M}_2Q)^{-1}Kf_4 \qquad (37)$$

$$V\mathcal{M}_1(q_1T\,[A][B])^{-1} = -Kf_1 + U\mathcal{M}_1(q_1\mathcal{M}_2T)^{-1}Kf_4 \qquad (38)$$

From the above it is seen that all transition probabilities can be determined. Therefore, the average times F_A, F^*_A, F_B, F^*_B and the probability P(C) can be calculated too. It is essential to note that these problems are solved by the suggested method without a prelimenary determination of K.

The constants q_1, q_2, Kf_1, Kf_2, Kf_3 and Kf_4 can be calculated by this method as well. Important conclusions for the monomers reactivities before and after being involved in the DAC to the propagating ends can be drawn from the values of these constants. The ratios $q_1Kf_1/Kf_2 = k_{AAB}/k_{ABA}$ and $q_2Kf_3/Kf_4 = k_{BBA}/k_{BAB}$ are of interest in this context. More profound information in this direction can be obtained after the prelimenary determination of K.

As an example the probability P(C) of the methyl acrylate (A) - 1,1-diphenylethylene (B) copolymerization (ITO and YAMASHITA 1966) has been calculated. In the case of B_* not adding to ~B• (HAM 1964) $q_2 = 0$, $Kf_3 = 0$, $p_{BB} = 0$ and $p^*_{BB} = 0$. The probabilities p_{AA} and p_{AB} has been calculated from the expressions (32) and (34). In order to determine Kf_2 and Kf_4 the expressions for p^*_{AA} (12) and p_{BA} (17) are substituted in the expression for m_{BAB} (31), yielding the equation

$$r = (uKf_2 + v)Kf_4 + wKf_2 \qquad (39)$$

where $r = (m_{BAB} - m_Bp_{AB})\mathcal{M}_1$, $u = (m_B - m_A)\,[A][B]^2$,
$v = (m_B - m_{BAB})\mathcal{M}_1$ and $w = m_B[A][B]$. Then

$Kf_2 = (b \pm (b^2 - 4ac)^{0,5})/2a$ and $Kf_4 = (r\ wKf_2)/(uKf_2 + v)$ where $a = u_1w_2 - w_1u_2$, $b = r_2u_1 + w_1v_2 - w_2v_1 - r_1u_2$ and $c = r_1v_2 - r_2v_1$ are calculated from the triad composition of two copolymers. $q_1 = 0,14$, $Kf_1 = 0,107$, $Kf_2 = 0,110$ and $Kf_4 = 0,40$ have been found. Other results are presented in TABLE 1.

TABLE 1

Average times of occurrence of the propagating chains in the states $\sim A^{\bullet}(F_A)$, $\sim A^{\bullet *}$ (F_A^*), $\sim B^{\bullet}(F_B)$, $\sim B^{\bullet *}$ (F_B^*) and probability for a donor-acceptor complexe participation in the copolymerization (P(C)) between methyl acrylate (A) and 1,1-diphenylethylene (B) from the triad composition of copolymers (ITO and YAMASHITA 1966). Temperature: 60°C. Initiator:benzoyl peroxide.

N	$x=\frac{A}{B}$	$y=\frac{m_A}{m_B}$	m_{AAA}	m_{BAB}	F_A	F_A^*	F_B	F_B^*	P(C)
1	9,04	1,79	0,128	0,205	0,605	0,037	0,260	0,098	0,270
2	13,30	2,17	0,189	0,135	0,665	0,010	0,209	0,106	0,232
3	24,10	3,23	0,367	0,076	0,748	0,016	0,175	0,061	0,154
4	61,30	5,40	0,591	0,059	0,796	0,048	0,124	0,032	0,160

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