Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Sawada, Hideo(1973) 'Heat of Terpolymerization', Journal of Macromolecular Science, Part A, 7: 4, 905 — 912
To link to this Article: DOI: 10.1080/00222337308061179
URL: http://dx.doi.org/10.1080/00222337308061179

J. MACROMOL. SCI.—CHEM., A7(4), pp. 905-912 (1973)

Heat of Terpolymerization

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ABSTRACT

A novel correlation for predicting the heat of terpolymerization from the binary data is proposed. This correlation is applicable to the ternary system with monomers which obey the Q-e scheme. The heat of terpolymerization for the ternary system methyl methacrylate-styrene-acrylonitrile is calculated from binary data.

INTRODUCTION

Alfrey and Lewis [1] developed a mathematical treatment relating the heat of binary copolymerization with the composition of the copolymer in terms of the molar enthalpies of the four basic propagation steps. In the previous paper [2] we related the heat of binary copolymerization to the heats of homopolymerization, the polymer composition, and two parameters which characterize the alternation tendency in copolymerization.

Heats of copolymerization were obtained for several binary systems [3-6]. Since no data are available for the ternary system and such data are more difficult to obtain than data for binary system, it is desirable to develop a method for the prediction of the heat of terpolymerization system from binary data.

THEORETICAL

The quantitative treatment of terpolymerization is quite complex since nine propagation reactions are involved.

Reaction	Heat of reaction
$M_1\cdot + M_1 \rightarrow M_1\cdot$	H_{11}
$M_1\cdot + M_2 \rightarrow M_2\cdot$	H_{12}
$M_1\cdot + M_3 \rightarrow M_3\cdot$	H_{13}
$M_2\cdot + M_1 \rightarrow M_1\cdot$	H_{21}
$M_2\cdot + M_2 \rightarrow M_2\cdot$	H_{22}
$M_2\cdot + M_3 \rightarrow M_3\cdot$	H_{23}
$M_3\cdot + M_1 \rightarrow M_1\cdot$	H_{31}
$M_3\cdot + M_2 \rightarrow M_2\cdot$	H_{32}
$M_3\cdot + M_3 \rightarrow M_3\cdot$	H_{33}

The expression for the molar heat of reaction of each of the propagation reactions is shown above. An expression for the heat of terpolymerization at low conversion can be obtained by a treatment similar to that used in binary copolymerization [2].

The molar heat of terpolymerization is given by

$$\Delta H_t = \frac{N_{11}}{N_0} H_{11} + \frac{N_{22}}{N_0} H_{22} + \frac{N_{33}}{N_0} H_{33} + \frac{N_{12}}{N_0} H_{12} + \frac{N_{21}}{N_0} H_{21}$$

$$+ \frac{N_{13}}{N_0} H_{13} + \frac{N_{31}}{N_0} H_{31} + \frac{N_{23}}{N_0} H_{23} + \frac{N_{32}}{N_0} H_{32} \qquad (1)$$

where the number of nearest-neighbor pairs of i and j is N_{ij}, and the total number of pairs in the copolymer is N_0. The number of

M_1 monomer units in the copolymer is N_0X_1, and thus the total number of M_1M_1 pairs is

$$N_{11} = N_0X_1P_{11} \tag{2}$$

where X_1 is the mole fraction of the monomer units M_1, and P_{11} is the conditional probability that M_1 monomer unit will follow M_1 monomer unit in the presence of M_3 monomer unit. Similarly, we have

$$N_{22} = N_0X_2P_{22} \tag{3}$$

$$N_{33} = N_0X_3P_{33} \tag{4}$$

$$N_{12} = N_0X_1P_{12} \tag{5}$$

$$N_{21} = N_0X_2P_{21} \tag{6}$$

$$N_{13} = N_0X_1P_{13} \tag{7}$$

$$N_{31} = N_0X_3P_{31} \tag{8}$$

$$N_{23} = N_0X_2P_{23} \tag{9}$$

$$N_{32} = N_0X_3P_{32} \tag{10}$$

where X_i is the mole fraction of M_i monomer unit, and P_{ij} is the conditional probability that the M_i monomer unit selected at random will be followed by the M_j monomer unit. The value of P_{ij} may be calculated from rate constant k as

$$P_{ij} = \frac{k_{ij}[M_i^*][M_j]}{k_{ij}[M_i^*][M_j] + k_{ii}[M_i^*][M_i] + k_{ik}[M_i^*][M_k]} \tag{11}$$

where i, j, and k have values of 1, 2, or 3. Combining Eqs. (2)-(10) with Eq. (1), we obtained

$$\Delta H_t = X_1P_{11}H_{11} + X_2P_{22}H_{22} + X_3P_{33}H_{33} + X_1P_{12}H_{12} + X_2P_{21}H_{21}$$

$$+ X_1P_{13}H_{13} + X_3P_{31}H_{31} + X_2P_{23}H_{23} + X_3P_{32}H_{32} \quad (12)$$

Ham [7] has treated the problem of terpolymer composition by making the simple assumption that the probability of producing a certain sequence of monomers is the same as producing the exact reverse sequence. This relationship of product probabilities is as follows:

$$P_{12}P_{23}P_{31} = P_{13}P_{32}P_{21} \quad (13)$$

A similar concept may be expressed as [8]:

$$X_1/X_j = P_{j1}/P_{1j} \quad (14)$$

Equations (13) and (14) have undergone some debate in the literature [9-12], but they are a necessary consequence of the Q-e scheme and can be derived from it. It is the purpose of this paper to evaluate the heat of terpolymerization with monomers which do obey the Q-e scheme.

Since we are dealing with monomers which obey the Q-e scheme, we find

$$X_1P_{12} = X_2P_{21} \quad (15)$$

$$X_1P_{13} = X_3P_{31} \quad (16)$$

$$X_2P_{23} = X_3P_{32} \quad (17)$$

Substitution of Eqs. (15), (16), and (17) into Eq. (12) yields

$$\Delta H_t = X_1P_{11}H_{11} + X_2P_{22}H_{22} + X_3P_{33}H_{33} + X_1P_{12}(H_{12} + H_{21})$$

$$+ X_1P_{13}(H_{13} + H_{31}) + X_2P_{23}(H_{23} + H_{32}) \quad (18)$$

In the present case for an infinite molecular weight terpolymer

$$P_{11} + P_{12} + P_{13} = 1 \tag{19}$$

$$P_{21} + P_{22} + P_{23} = 1 \tag{20}$$

$$P_{31} + P_{32} + P_{33} = 1 \tag{21}$$

Thus Eq. (18) can be expressed in terms of the probabilities of cross-propagation:

$$\begin{aligned}\Delta H_t = {} & H_{11}X_1 + H_{22}X_2 + H_{33}X_3 \\ & + X_1P_{12}(H_{12} - H_{11}) - X_2P_{21}H_{22} + X_1P_{12}H_{21} \\ & + X_1P_{13}(H_{13} - H_{11}) - X_3P_{31}H_{33} + X_1P_{13}H_{31} \\ & + X_2P_{23}(H_{23} - H_{22}) - X_3P_{32}H_{33} + X_2P_{23}H_{32}\end{aligned} \tag{22}$$

Upon substitution of Eqs. (15)-(17) into Eq. (22), we find

$$\begin{aligned}\Delta H_t = {} & H_{11}X_1 + H_{22}X_2 + H_{33}X_3 \\ & + X_1P_{12}[(H_{12} + H_{21}) - (H_{11} + H_{22})] \\ & + X_1P_{13}[(H_{13} + H_{31}) - (H_{11} + H_{33})] \\ & + X_2P_{23}[(H_{23} + H_{32}) - (H_{22} + H_{33})]\end{aligned} \tag{23}$$

Defining Ω_{ij} as [13, 14]

$$\Omega_{ij} = (H_{ij} + H_{ji}) - (H_{ii} + H_{jj}) \tag{24}$$

Consequently, the heat of terpolymerization is given by

$$\begin{aligned}\Delta H_t = {} & H_{11}X_1 + H_{22}X_2 + H_{33}X_3 + X_1P_{12}\Omega_{12} + X_1P_{13}\Omega_{13} \\ & + X_2P_{23}\Omega_{23}\end{aligned} \tag{25}$$

The heat of terpolymerization for the ternary system acrylonitrile (AN = 1) - styrene (ST = 2) - methyl methacrylate (MMA = 3) calculated from Eq. (25) are presented in Fig. 1. Values in Fig. 1 are obtained by using [4]

$r_{12} = 0.18$, $r_{21} = 1.35$, $r_{13} = 0.04$, $r_{23} = 0.46$,

$H_{11} = 16.74$ kcal/mole, $H_{22} = 13.42$ kcal/mole

$H_{33} = 16.29$ kcal/mole

and Ω_{ij} are shown in Table 1. Ham [15] has found that Eq. (13) can be applied to this ternary system. Thus it is possible to predict the heat of terpolymerization in this system from binary data.

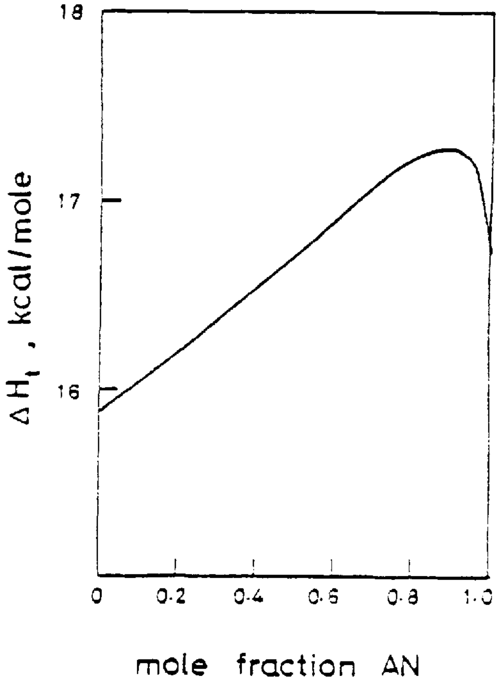

FIG. 1. Heat of terpolymerization for the acrylonitrile-methyl methacrylate-styrene system: (mole MMA)/(mole ST) = 1.

TABLE 1. Parameters Used in Predicting the Heat of Terpolymerization

Binary system	$H_{ij} + H_{ji}$ (kcal/mole)	$H_{ii} + H_{jj}$ (kcal/mole)	Ω_{ij} (kcal/mole)
AN-MMA	28.4[a]	30.4[a]	-2.00
AN-ST	34.67[a]	32.76[a]	+1.91
MMA-ST	32.74[b]	29.74[b]	+3.00

[a] Data from Ref. 4.
[b] Data from Ref. 3.

In the case of binary copolymerization X_3, Ω_{13}, Ω_{23}, P_{13}, and P_{23} will vanish. In this case Eq. (25) will reduce to Eq. (26), which is identical to Alfrey's [1]:

$$\Delta H = H_{11}X_1 + H_{22}X_2 + P_{12}\Omega_{12}X_1 \tag{26}$$

Using the same procedure as for the heat of terpolymerization in Eq. (25), the following equations are found in the case of multicomponent copolymerization containing n monomers which obey the Q-e scheme.

$$\begin{aligned}\Delta H = {} & H_{11}X_1 + H_{22}X_2 + H_{33}X_3 + \dots + H_{nn}X_n \\ & + X_1P_{12}\Omega_{12} + X_1P_{13}\Omega_{13} + \dots + X_1P_{1n}\Omega_{1n} \\ & + X_2P_{23}\Omega_{23} + X_2P_{24}\Omega_{24} + \dots + X_2P_{2n}\Omega_{2n} \\ & + X_3P_{34}\Omega_{34} + X_3P_{35}\Omega_{35} + \dots + X_3P_{3n}\Omega_{3n} \\ & + \dots \\ & + X_{n-1}P_{n-1,n}\Omega_{n-1,n}\end{aligned} \tag{27}$$

Equation (27) gives the heat of multicomponent copolymerization with n monomers, and this equation is only applicable to multicomponent systems for which copolymerization follows the Q-e scheme. Similar expressions hold for entropy and free energy changes with n monomers which obey the Q-e scheme.

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Received for publication October 10, 1972