

STUDY OF THE TEMPERATURE DEPENDENCE OF THE COPOLYMERIZATION CONSTANTS FOR STILBENE WITH STYRENE AND ACENAPHTHYLENE*

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The temperature dependence of the binary radical copolymerization constants has been investigated for stilbene with styrene and acenaphthylene in the temperature interval 70–140°. The difference between the activation energies and entropies has been determined as well as the ratio of preexponential factors for the rate constants of elementary steps of chain propagation. The influence of the steric effect on the addition of the stilbene monomer and radical during chain propagation has been demonstrated. The preexponential factors and steric factors have been estimated for rate constants of elementary propagation steps for the system stilbene–styrene.

INVESTIGATIONS of the temperature dependence of copolymerization should to some extent provide information as to which structural factors influence the reactivity of monomers in copolymerization reactions [1, 2]. This method of investigation is of particular interest in the case of pairs monomers differing markedly in their reactivity, for which $10 < r < 0.1$, since one must expect to find temperature having the most significant influence on copolymerization constants [1–3] where monomers of this type are concerned. However reports currently available [2, 4–9] show the very limited extent to which systems of the type in question have been investigated.

Our aim was to investigate the temperature dependence of binary radical copolymerization constants for stilbene (M_2) with styrene (M_1) and acenaphthylene (M_1), and to use the results obtained to determine the influence of the steric effect on the copolymerization of stilbene.

The characteristics of the starting substances (styrene, acenaphthylene, *trans*-stilbene, azobisisobutyronitrile (AIBN) and dimethylformamide (DMF) were as stated in [10]. Ditolylmethane (DTM) was purified by the method of [11], and had m.p. 30°, b.p. 298°, n_D^{20} 1.5665, d_4^{20} 0.9870.

Copolymerization of stilbene with styrene and acenaphthylene was carried out in DMF at 110° and in DTM at 140°. The copolymerization procedure was as carried out at 70° [10]. As in the case of the copolymerization of stilbene with styrene in DMF and toluene at 70° we first of all verified that the solvent did not influence the behaviour of the systems under study in copolymerization reactions. As in [5–8], the initiator at all temperatures was AIBN, 1.75% on the weight of monomers. Since the breakdown time for

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the initiator decreases markedly as the temperature rises, we considerably curtailed the polymerization times at 110 and 140° (to 0.5–1.0 hr at 140°). The total concentration of monomers in solution amounted to 10 wt.%. Analysis of the monomers was carried out polarographically for acenaphthylene and stilbene, and by a mercury–acetate method for styrene, as in [10].

Table 1 gives the data obtained for stilbene copolymerization with styrene and acenaphthylene at 110 and 140°. At all the temperatures investigated plots of the composition of initial mixtures of monomers were identical for both systems and were similar to those obtained in the case of copolymerization at 70° [10]. As the temperature rises, the stilbene concentration in the copolymer composition decreases in both systems.

TABLE 1. DATA ON THE COPOLYMERIZATION OF STILBENE (M_2) AT TWO TEMPERATURES

M_2^0 , mole fractions	M_2 , mole fractions	m_2 , mole %	M_2^0 , mole fractions	M_2 , mole fractions	m_2 , mole %
Styrene–stilbene (110°)			Acenaphthylene–stilbene (110°)		
0.100	0.091	2.6	0.099	0.086	3.3
0.198	0.180	5.1	0.202	0.186	4.0
0.348	0.320	8.7	0.350	0.326	8.0
0.502	0.464	14.8	0.498	0.466	13.8
0.647	0.602	21.7	0.653	0.620	18.6
0.802	0.757	30.2	0.805	0.772	27.3
0.901	0.854	44.3	0.907	0.850	39.3
Styrene–stilbene (140°)			Acenaphthylene–stilbene (140°)		
0.101	0.086	2.5	0.108	0.095	2.0
0.199	0.176	4.4	0.214	0.194	3.4
0.348	0.302	10.3	0.370	0.329	8.3
0.501	0.448	15.0	0.520	0.468	12.8
0.648	0.608	17.0	0.671	0.625	16.0
0.802	0.754	25.4	0.817	0.763	27.5
0.901	0.861	37.0	0.914	0.881	35.5

Table 2 contains the copolymerization constants calculated from the data in Table 1 with the aid of an integral equation of copolymer composition using a graphic method based on the Shtraikhman approach [12]. For comparison Table 2 also gives the copolymerization constants previously determined by us for the systems under study at 70° [10].

The results obtained show that as the temperature rises, identical changes in the copolymerization constants occur in both systems: values of r_1 and r_2 increase and decrease respectively, and tend to diverge still further from unity. This is apparent from the Figure where, as an example, we have plots of $\log r_1$ and $\log r_2$ vs. $1/T$ for the styrene–stilbene system.

Using $\log r$ vs. $1/T$ plots together with regressive analysis as [13] we calculated (Table 2) differences between activation energies and entropies for pro-

pagation steps taking place as in the homopolymerization of monomers (monomer M_1 is added to the $\sim R_1$ radical, and M_2 is added to $\sim R_2$) along with cross addition of monomers to radicals (M_1 to $\sim R_2$ and M_2 to $\sim R_1$), and in addition we obtained ratios of preexponential factors A_{11}/A_{12} for rate constants k_{11} and k_{12} for the reactions in question, viz. $A_{11}/A_{12} = P_{11} Z_{11}/P_{12} Z_{12}$ [1, 14], where P_{ij} is the steric factor for the propagation reaction, Z_{ij} is the collision factor, showing the collision probability in the course of 1 sec for two reacting particles in a 1 cm³ volume.

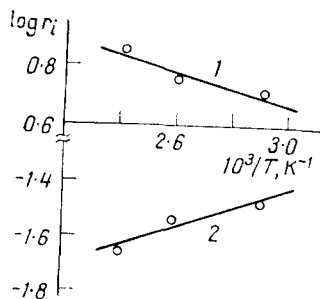
TABLE 2. KINETIC PARAMETERS OF THE TEMPERATURE DEPENDENCE OF THE COPOLYMERIZATION CONSTANTS FOR STILBENE (M_2) WITH STYRENE (M_1) AND ACENAPHTHYLENE (M_1)

M_1^*	Copolymerization constants at T°			$E_{11}-E_{12}$, kJ/mole	$\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger$, J/mole-deg.	A_{11}/A_{12}
	70	110	140			
Styrene	5.17 ± 0.30	5.76 ± 0.33	7.23 ± 0.45	5.5 ± 1.4	29.4 ± 4.8	34.34
Stilbene	0.033 ± 0.070	0.029 ± 0.060	0.022 ± 0.55	-6.6 ± 2.2	-47.4 ± 5.9	3.38×10^{-3}
Acenaphthyl- ene	5.38 ± 0.18	7.34 ± 0.19	11.23 ± 0.66	11.9 ± 2.6	48.5 ± 6.8	339.0
Stilbene	0.027 ± 0.034	0.012 ± 0.033	0.007 ± 0.064	-22.2 ± 0.5	-94.8 ± 1.7	1.13×10^{-5}

* Each monomer in the pair is examined in turn as monomer M_1 .

It can be seen from the Figure that the angle is considerable for the linear temperature of copolymerization constants r_1 and r_2 , and that the values of $(E_{11}-E_{12})$ and $(E_{22}-E_{21})$ (see Table 2) are fairly high for both systems. Moreover, it appears from the signs of the values in question that there will be preferential addition of monomer M_2 , compared with monomer M_1 , to both types of polymeric radicals ($\sim R_1$ and $\sim R_2$) in each system. This means that the total reactivity of the stilbene monomer must be slightly higher than for the styrene and acenaphthylene, probably as a result of a higher conjugation energy [15].

When extrapolated curves of the temperature dependence do not go through the coordinate origin, but make considerable intercepts on the ordinate axis



Plots of $\log r_1$ (1) and $\log r_2$ (2) vs. $1/T$ for the case of styrene copolymerization with stilbene (M_2).

(see Figure). There are high absolute values for differences in the activation entropies of competing propagation reactions, and there are differences of several orders of magnitude in the preexponential factors for rate constants of the reactions under study (Table 2). All these considerations point to a significant steric effect involved in the reactions. Moreover in each system the values of $(\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger)$ and A_{11}/A_{12} evidence a predominance of reactions of homopolymerization of M_1 monomers (styrene, acenaphthylene), while the values of $(\Delta S_{22}^\ddagger - \Delta S_{21}^\ddagger)$ and A_{22}/A_{21} point to preferential cross addition of monomer M_1 to the stilbene $\sim R_2^\cdot$ radical.

In view of the r_1 and r_2 values, as well as the differences in the activation energies and entropies one may conclude that the steric factor has a determining influence in the copolymerization of both the systems under study, and that owing to the steric effect the higher reactivity of stilbene is not realized. At the same time the steric hindrances are smallest in propagation reactions involving homopolymerization of M_1 monomers, M_2 addition to $R_2^\cdot \sim$ are sterically more inhibited than M_1 addition to $\sim R_1^\cdot$ and M_2 addition to $\sim R_2^\cdot$ is more inhibited than M_1 addition to $\sim R_2^\cdot$. In view of the fact that stilbene does not homopolymerize by a radical mechanism [1, 2], one may surmise that steric hindrances will be greatest in the case of M_2 addition to $\sim R_2^\cdot$.

TABLE 3. RESULTS OF CALCULATION OF STERIC FACTORS FOR STILBENE (M_2) COPOLYMERIZATION WITH STYRENE (M_1) BASED ON A COLLISION THEORY [14]

Type of addition	$\bar{u} \times 10^{-4}$ *, cm/sec	Collision section $\sigma \times 10^{14}$, cm	$Z \times 10^{10}$, cm ³ /sec	$P \times 10^7$	$A = PZ \times 10^{16}$, cm ³ /sec
$M_1 + \sim R_1^\cdot$	3.74	1.28	4.77	325.6	155.3
$M_2 + \sim R_1^\cdot$	3.32	1.45	4.81	9.401	4.523
$M_1 + \sim R_2^\cdot$	3.32	1.54	5.11	9.401	4.804
$M_2 + \sim R_2^\cdot$	2.84	1.73	4.91	0.0331	0.01625

* Average relative rate of motion of the monomer and of the end of the radical at 70°.

To determine the magnitude of the steric effect for each elementary reaction of chain propagation during copolymerization one has to know the rate constants of homopolymerization reactions k_{11} and k_{22} and for monomers M_1 and M_2 , which would enable one to calculate rate constants for cross propagation reactions k_{12} and k_{21} . In the case of our systems this could not be done owing to the inability of stilbene to homopolymerize by a radical mechanism.

However, we attempted to determine the preexponential factors A_{ij} and steric factors P_{ij} for rate constants of elementary propagation reactions for the system styrene–stilbene, for which k_{11} for styrene is known to be $9.35 \times 10^6 \exp [-7250/RT]$ [15], in line with the collision theory and using the formulae

in [14], assuming that steric factors for the cross propagation reactions are approximately equal, i.e. $P_{12} \simeq P_{21}$.

The basis of the latter assumption is the Alfrey theory [1], according to which steric hindrances in the transition state of the propagation reaction appear as a result of interaction between substituents of penultimate C atoms of the radical with substituents of the bond-forming C atom in monomer molecules.

Although it may be assumed that M_2 addition to $\sim R_1^\cdot$ will mean that the value of the steric factor will be slightly higher than for M_1 addition to $\sim R_2^\cdot$, the activation entropy loss is higher in the former case, because the structurally more complex stilbene molecule must lose a larger number of degrees of freedom in the transition state of the propagation reaction than the styrene molecule.

However our assumption that steric factors are equal for the cross propagation reactions allows us, as may be seen from Table 3, to determine the steric factor and the preexponential factor for the rate of the stilbene homopolymerization reaction, which it is practically impossible to carry out.

At the same time in calculating parameter Z_{ij} [14] in accordance with the collision theory for two colliding particles (the polymeric radical end and the monomer molecule), we took as molecular weights those of the monomers (styrene, stilbene) and of the final unit of the radical, while the density values adopted were those of the monomers and polymers (polystyrene, stilbene) at 70°.

It can be seen from Table 3 that the calculated hypothetical preexponential factor A_{22} and steric factor P_{22} for the stilbene homopolymerization rate constant are rather low. The values are lower by four orders than the corresponding values for styrene homopolymerization, while the preexponent A_{21} is 547 times less than that for the homopolymerization of a readily polymerizing monomer, methyl methacrylate ($A_{MMA} = 8.884 \times 10^{-16}$ cm³/sec [15]).

This means that despite the approximate character of the description of the radical copolymerization reaction involving use of the collision theory, and despite the assumption as to the equality of P_{12} and P_{21} and the fairly large errors in determining constants r_2 , as is normally the case for systems of the type in question [1], we may, in view of the values obtained for P_{22} and A_{22} conclude that the steric effect is the main reason for the inability of stilbene to homopolymerize by a radical mechanism.

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POLYURETHANES PREPARED FROM OXYPROPYLATED LIGNIN*

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The oxypropylation of technical lignins in glycerin medium has been investigated. It was found that on raising the temperature above 100° the difference in the reactivities of phenolic and aliphatic OH groups in the oxypropylation of hydrolyzed lignin and lignosulphonates decreases. It is shown that oxypropylation products of the specified types of lignin are oligoethers with a polymodal molecular weight distribution function and a polydispersity parameter of more than 5. As a result of oxypropylation the reactivity of lignins is significantly increased with respect to isocyanates, which means that these materials are suitable for use in the preparation of polyurethane foams and coatings.

FROM the point of view of the practical exploitation of lignin, which is a multi-tonnage waste product of the cotton-cellulose and hydrolyzing manufacturing processes, major significance is attached to lignopolyurethanes, which are prod-

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