

## Kinetic Studies on Copolycondensation Processes.

### II. Isokinetic Temperature

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#### Synopsis

Assuming the applicability of the Arrhenius equation to the polycondensation processes, two-by-two homopolycondensation processes proceeding with one of the monomers—the same in both cases—were examined. It was considered whether there is a temperature at which the reactivity of the two different monomers becomes the same. The isokinetic temperatures for four different systems were determined experimentally, and it was found that they are within an accessible experimental range.

As is known, properties of copolymers depend not only on their composition but also, to a considerable extent, on heterogeneity of composition and chemical structure of particular macromolecules. This concerns also products of copolycondensation.

Let us consider a simple case of copolycondensation of three bifunctional monomers A, B, and C so selected that functional groups of monomer A react with functional groups of monomers B and C, while functional groups of B and C are unable to react between themselves. If the copolycondensation is carried out under such conditions where the probability of interchain exchange is respectively low and the following condition is satisfied:

$$c_{A_0} = c_{B_0} + c_{C_0} \quad (1)$$

where  $c_{A_0}$ ,  $c_{B_0}$ , and  $c_{C_0}$  are the original concentrations of functional groups of monomers A, B, and C, respectively, then one may assume that the distribution of bonds A-B and A-C along chains of the macromolecules formed as well as the composition of copolymer being formed at various stages of the process will be dependent on the reactivity of functional groups of monomers B and C in their reaction with functional groups of monomer A. At high differences in the rate constants of reactions between A and B, and between A and C, one should expect a relatively high portion of the more reactive component in the macromolecules being formed in the case of low extents of reaction. This portion will decrease with a lowering in the difference in reactivities of monomers B and C, and the distribution of B and C units along macromolecule chains will be approaching a random distribution. Simultaneously, chemical composition of the product being formed at any stage of the process will approach more and more the composition of the original monomer mixture.

In a particular case when the rate constants of homopolycondensation are equal to each other, the distribution of B and C units should be random, with the composition of copolymer being the same for any extent of reaction. The equation given previously,<sup>1</sup>

$$\frac{dp}{dt} = (1 - p)[k_{AB}(c_{B_0} - c_{B_k}) + k_{AC}(c_{C_0} - c_{C_k})] \quad (2)$$

where  $p$  is the extent of the reaction,  $k_{AB}$  and  $k_{AC}$  are rate constants for homopolycondensations, and  $c_{B_k}$  and  $c_{C_k}$  are the concentrations of reacted functional groups of B and C, may then take the following form:

$$\frac{dp}{dt} = kc_0(1 - p)^2 \quad (3)$$

where  $k = k_{AB} = k_{AC}$  and  $c_0 = c_{A_0} = c_{B_0} + c_{C_0}$ , thus, the form of kinetic equation describing the homopolycondensation process.

The assumption of the effect of reactivity on the copolymer composition and macromolecule chain structure is confirmed by the data obtained for the copolycondensation of terephthaloyl chloride, bisphenol A, and bisnaphthol.<sup>2</sup>

These considerations and observations lead to a conclusion that, having three monomers A, B, and C, it is possible to obtain copolymers of the same composition but of different structure of macromolecule chains if one could control the relative reactivity of monomers by altering the reaction conditions.

As is known, temperature is a parameter which affects directly the value of rate constant. If both homopolycondensation reactions satisfy the known relationship of Arrhenius and their activation energies are different, there should be a temperature at which the rate constants are equal to each other. The point of intersection of straight lines in the system of  $\ln k = f(1/T)$  marks the reciprocal value of this temperature.

The isokinetic temperature for copolycondensation may be given by the equation

$$T_i = \frac{E_{AB} - E_{AC}}{R(B_{AB} - B_{AC})} \quad (4)$$

where  $E_{AB}$  and  $E_{AC}$  are the activation energies of homopolycondensations,  $R$  is the universal gas constant, and  $B_{AB}$  and  $B_{AC}$  are the preexponent factors in the Arrhenius equation.

If at temperatures lower than  $T_i$ ,  $k_{AB} > k_{AC}$ , then after raising the temperature above  $T_i$  monomer C becomes more active in the reaction with monomer A than monomer B.

It is thus clear that the distribution of B and C units along the macromolecule chains should vary considerably with varying temperature of the process within the range including the isokinetic temperature. Particularly, at the isokinetic temperature, there should be formed a product of

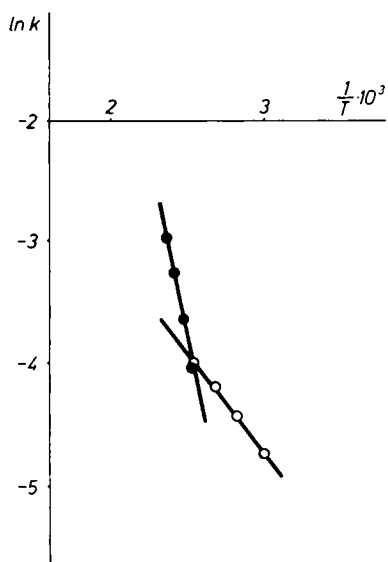


Fig. 1. Straight lines in the Arrhenius system: (○) bisphenol A and its bischlorformate; (●) bisphenol A and bischlorformate of 1,8-octanediol.

invariant composition independent of the extent of reaction and of random distribution of B and C units.

Possibility for the isokinetic temperature to occur is beyond doubt from the theoretical point of view, but  $T_i$  makes physical sense only within the range of temperatures where neither the substrates nor the products of copolycondensation undergo thermal decomposition, and the process itself proceeds at a measurable rate.

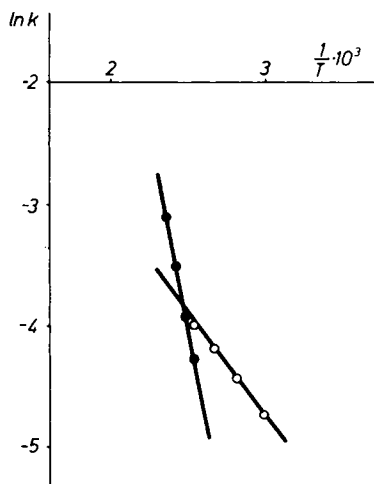


Fig. 2. Straight lines in the Arrhenius system: (○) bisphenol A and its bischlorformate; (●) 1,8-octanediol and bischlorformate of bisphenol A.

To verify whether the isokinetic temperature is within such a range under real conditions, measurements of kinetic constants were made at various temperatures for homopolycondensation of selected pairs of monomers. The rate constants and activation energies were determined for the process of obtaining of polycarbonate from (1) bisphenol A and its bischlorformate; (2) bisphenol A and bischlorformate of 1,8-octanediol; (3) 1,8-octanediol and bischlorformate of bisphenol A; and (4) 1,8-octanediol and its bischlorformate.

The processes were carried out in homogeneous systems in nitrobenzene. The original concentrations of functional groups were 0.2 mole/l.

Using three instead of two of the mentioned monomers, we shall deal with the copolycondensation of the type under investigation. Each of the monomers may play the part of monomer A in the process. If then, in the cases considered, the isokinetic temperature is within the range accessible in experiments, the straight lines in the Arrhenius system for selected pairs of monomers should intersect each other within this range.

Typical systems are shown in Figures 1 and 2.

The values of the isokinetic temperatures found for all the four possible cases of copolycondensation of the monomers used are given in Table I.

TABLE I  
The Values of the Isokinetic Temperatures for Investigated Systems

Monomer A	Monomer B	Monomer C	$T_i$ , °C
Bisphenol A	bischlorformate of bisphenol A	bischlorformate of 1,8-octanediol	121
1,8-Octanediol	bischlorformate of bisphenol A	bischlorformate of 1,8-octanediol	203
Bischlorformate of bisphenol A	bisphenol A	1,8-octanediol	130
Bischlorformate of 1,8-octanediol	bisphenol A	1,8-octanediol	214

As follows from the presented data, all the isokinetic temperatures found by us are within the range accessible in experiments. This fact, in our opinion, makes it possible for a new procedure to control the copolycondensation process by means of suitable selection of the reaction temperature.

### References

1. E. Turska, S. Boryniec, and L. Pietrzak, *J. Appl. Polym. Sci.*, **18**, 667 (1974).
2. E. Turska, *Vysokomol. Sojed.*, **15**, 393 (1973).

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