

Kinetic Studies on Copolycondensation Processes. IV. Chemical Composition of Copolycondensation Products

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Synopsis

The kinetics of polycondensation and copolycondensation of terephthaloyl chloride with numerous bisphenols in α -chloronaphthalene solutions were examined. The values of activation energy E of the polycondensation processes were calculated. Isokinetic temperatures for different systems of monomers were determined. A series of syntheses of copolyesters at isokinetic temperature and other temperatures was carried out. The products obtained during the reaction were examined. It was found that at isokinetic temperature the composition of the products is independent of the extent of reaction, whereas at other temperatures it depends on the reactivity ratio of monomers used, as well as on the extent of reaction.

INTRODUCTION

In previous papers¹⁻⁴ we presented the results of our investigations on the copolycondensation process in a solution. It was found that the composition of the formed product is not constant during the course of the reaction and depends on the reactivity of the used monomers and on the extent of reaction.³

According to our kinetic considerations,² the reactivities of monomers B and C with intermonomer A at the isokinetic temperature are equal. Thus it would be expected that the chemical composition of the copolycondensation product will be stable, independent of the extent of reaction, and equal to the initial composition of monomer mixture. At temperatures different from the isokinetic one, monomers have different reactivities, and it may be expected that the composition of the copolycondensation product changes as the extent of the reaction grows. The microstructure of copolymer molecules should also vary with the temperature of the copolycondensation reaction. The present work has been undertaken in order to make an experimental check of our predictions.

RESULTS AND DISCUSSION

The values of the rate constants of numerous bisphenols (Table I) in reactions with terephthaloyl chloride at various temperatures were determined. The homopolycondensation reactions were carried out in α -chloronaphthalene with the initial concentration of monomers of 0.1 mol/l in nitrogen. The extent of the reaction p was determined from the amount of hydrogen chloride, the by-

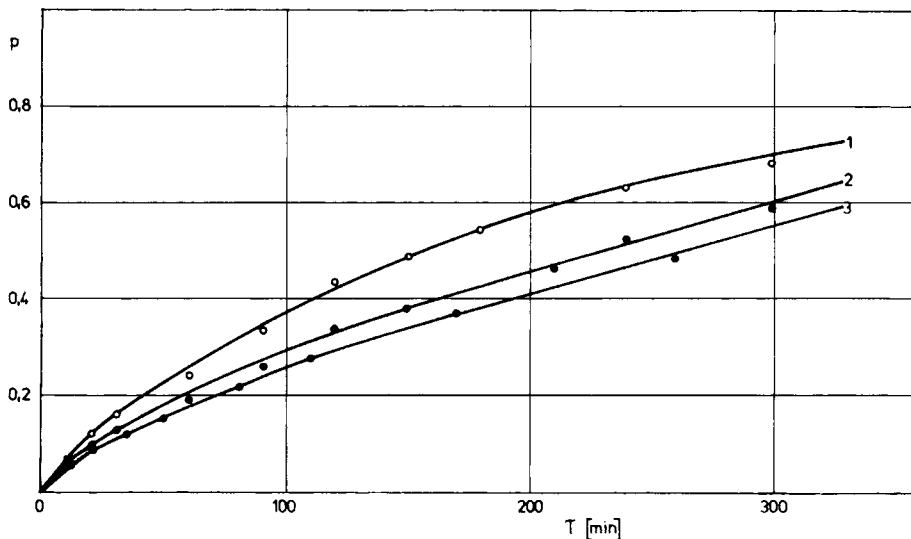


Fig. 1. Experimental curves of the relationship between the extent of reaction and time at 180°C: 1—polycondensation of terephthaloyl chloride and phenolphthaleine; 2—polycondensation of terephthaloyl chloride and dimethylbisphenol A; 3—polycondensation of terephthaloyl chloride and dichlorobisphenol A.

product of the reaction. The values of the average degree of polymerization \bar{P}_n , calculated from the experimental data, were linear functions of the duration of reaction in all the cases. This means that the polycondensation reaction of these bisphenols with terephthaloyl chloride is described by means of the second-order kinetic equation. Figure 1 presents some of the experimental curves as examples of the relationship between the extent of reaction and the duration of the polycondensation of terephthaloyl chloride with phenolphthaleine, dichlorobisphenol A, and dimethylbisphenol A at 180°C. Figure 2 shows the relationship between \bar{P}_n and the length of polycondensation for these same reactions. On the basis

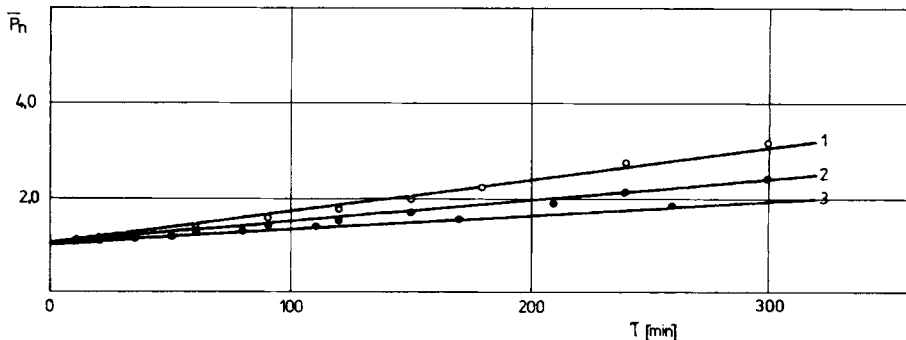


Fig. 2. Curves of the relationship between the average degree of polymerization \bar{P}_n and time of reaction at 180°C: 1—polycondensation of terephthaloyl chloride and phenolphthaleine; 2—polycondensation of terephthaloyl chloride and dimethylbisphenol A; 3—polycondensation of terephthaloyl chloride and dichlorobisphenol A.

TABLE I
Kinetic Constants of Reactions of Terephthaloyl Chloride with Various Bisphenols with Values of Activation Energy E and Preexponential Factor for These Reactions

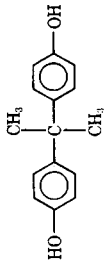
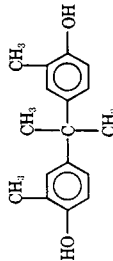
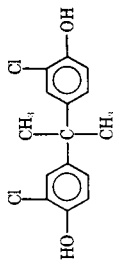
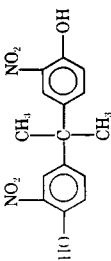
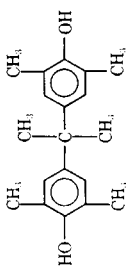
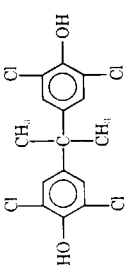
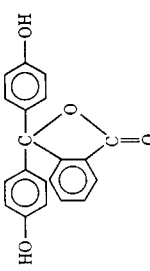
Bisphenol	Formula	$k \times 10^3$ (l mol ⁻¹ sec ⁻¹)				E (kcal/mol)	B	Ref.
		180°C	190°C	200°C	220°C			
Bisphenol A ^a		1.19	1.78	2.78	4.80	15.3	10.169	
Dimethylbisphenol A		0.49	0.85	1.29	4.10	23.6	18.435	5
Dichlorobisphenol A		0.36	0.56	1.01	2.03	19.2	13.271	6
Dinitrobisphenol A		0.08	0.15	0.25	0.68	23.7	16.736	7

TABLE I. Continued.

Bisphenol	Formula	$k \times 10^3$ (l mol ⁻¹ sec ⁻¹)			E (kcal/mol)	B	Ref.
		180°C	190°C	200°C			
Tetramethylbisphenol A		0.14	0.17	0.35	1.09	16.191	8
Tetrachlorobisphenol A		0.10	0.15	0.34	0.86	17.180	9
Phenolphthaleine ^a		0.64	0.89	1.29	2.50	9.321	

^a Commercial product purified by crystallization.

TABLE II
Isokinetic Temperatures for Bisphenol-Bisphenol Reactions with Terephthaloyl Chloride

Monomers	T_i	
	°K	°C
Bisphenol A-phenolphthaleine	118	-155
Bisphenol A-dimethylbisphenol A	502	229
Bisphenol A-tetramethylbisphenol A	614	341
Bisphenol A-dinitrobisphenol A	639	366
Bisphenol A-dichlorobisphenol A	628	355
Bisphenol A-tetrachlorobisphenol A	613	340
Phenolphthaleine-dimethylbisphenol A	473	200
Phenolphthaleine-tetramethylbisphenol A	553	280
Phenolphthaleine-dinitrobisphenol A	580	307
Phenolphthaleine-dichlorobisphenol A	515	242
Phenolphthaleine-tetrachlorobisphenol A	560	287
Dimethylbisphenol A-dinitrobisphenol A	—	—
Tetramethylbisphenol A-dinitrobisphenol A	927	654
Tetramethylbisphenol A-dimethylbisphenol A	203	-70
Tetramethylbisphenol A-dichlorobisphenol A	605	332
Tetramethylbisphenol A-tetrachlorobisphenol A	613	340
Dichlorobisphenol A-tetrachlorobisphenol A	607	334
Dimethylbisphenol A-dichlorobisphenol A	430	157
Dimethylbisphenol A-tetrachlorobisphenol A	—	—
Dichlorobisphenol A-dinitrobisphenol A	656	383
Tetrachlorobisphenol A-dinitrobisphenol A	228	-45

of the results, Arrhenius plots were drawn in the system of coordinates ($T^{-1} \times 10^3$) and $\log k$, where T is the temperature of reaction (°K), k is the kinetic constant of the homopolycondensation reaction at temperature T (in $\text{l mol}^{-1} \text{sec}^{-1}$). The energy of activation E and the pre-exponential factor B from the Arrhenius equation $k = B \exp(-E/RT)$ were calculated from the plots for each homopolycondensation reaction. The experimental data and results are given in Table I. The isokinetic temperature T_i for different monomer systems was evaluated from the point of intersection of two straight lines on the Arrhenius plot or calculated from the following equation²:

$$T_i = (E_{AB} - E_{AC})/R(B_{AB} - B_{AC})$$

Figure 3 presents the Arrhenius plots for the reactions of terephthaloyl chloride with phenolphthaleine, dichlorobisphenol A, and dimethylbisphenol A. All T_i values are presented in Table II.

In numerous cases it was physically impossible to carry out the process at the isokinetic temperature; however, the isokinetic temperature was attainable experimentally in a number of cases.

Two systems were chosen for further investigation:

System I: Phenolphthaleine (0.05 mol/l), dichlorobisphenol A (0.05 mol/l), and terephthaloyl chloride (0.1 mol/l) at reaction temperatures 180°C ($T < T_i$) and 242°C ($T = T_i$).

System II: Phenolphthaleine (0.05 mol/l), dimethylbisphenol A (0.05 mol/l), and terephthaloyl chloride (0.1 mol/l) at reaction temperatures 180°C ($T < T_i$), 200°C ($T = T_i$), and 220°C ($T > T_i$).

A series of copolyester syntheses at isokinetic and other temperatures was carried out in analogous conditions to those used for homopolycondensation.

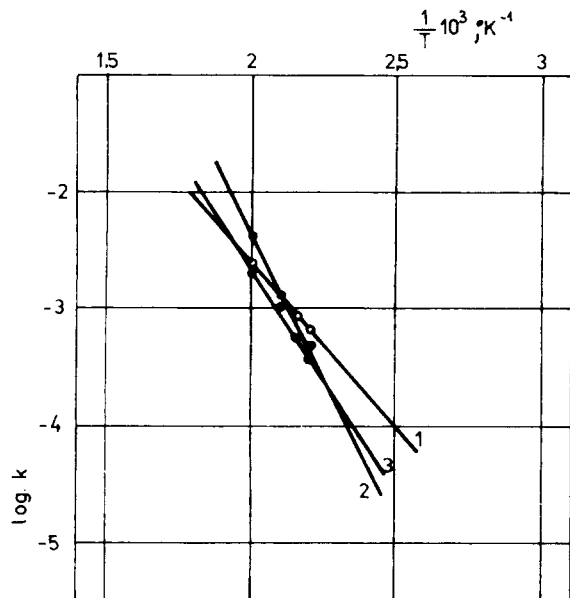


Fig. 3. Straight-line Arrhenius plots for 1—terephthaloyl chloride and phenolphthaleine; 2—terephthaloyl chloride and dimethylbisphenol A; 3—terephthaloyl chloride and dichlorobisphenol A.

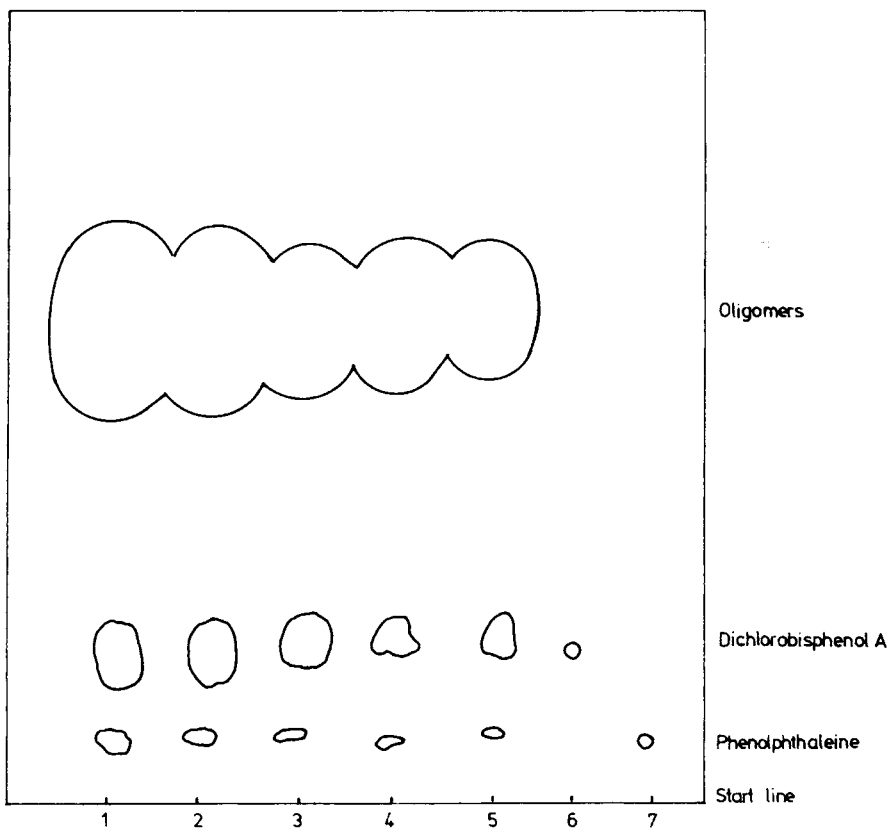


Fig. 4. Analysis of filtrates of copolyester samples obtained from terephthaloyl chloride, phenolphthaleine, and dichlorobisphenol A at 180°C ($T < T_i$): 1-5, filtrate after 1, 2, 4, 6, and 8 hr of reaction, respectively; 6, solution of dichlorobisphenol A; 7, solution of phenolphthaleine.

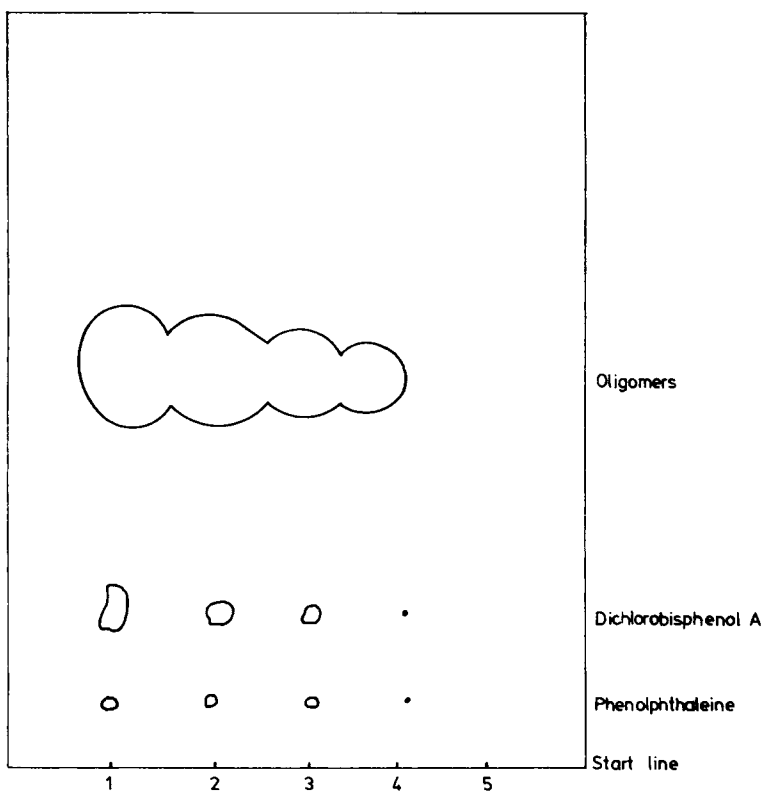


Fig. 5. Analysis of filtrates of copolyester samples obtained from terephthaloyl chloride, phenolphthaleine and dichlorobisphenol A at 242°C ($T = T_i$): 1-5, filtrate after 30, 70, 120, 140, and 360 min of reaction, respectively.

TABLE III
Chlorine Contents in Copolyester Samples from Terephthaloyl Chloride, Phenolphthaleine, and Dichlorobisphenol A and Extent of Reaction

Temp. (°C)	Time of Reaction (min)	Extent of Reaction (%)	Chlorine Contents (wt %)
180	120	28	4.90
	240	45	5.35
	360	56	5.59
	480	65	6.42
242	30	59	8.30
	70	85	8.59
	240	97	8.92
	360	99	8.91

The time dependence of the extent of reaction was determined for the copolycondensation reactions. Then copolycondensation was carried out in the identical way, and the samples of polymers were collected at predetermined times. The samples were precipitated with methyl alcohol, dried, and analyzed.

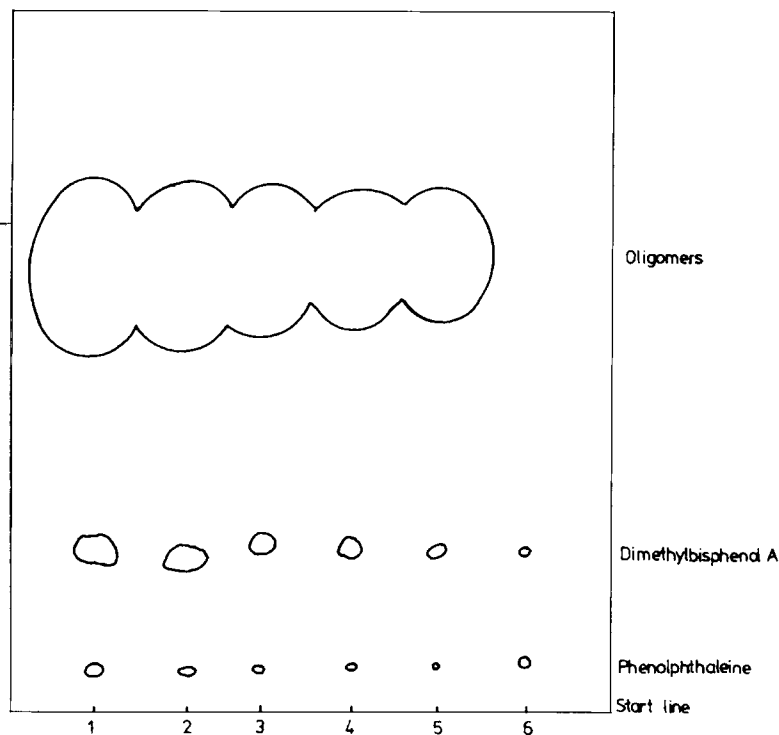


Fig. 6. Analysis of filtrates of copolyester samples obtained from terephthaloyl chloride, phenolphthaleine, and dimethylbisphenol A at 180°C ($T < T_i$): 1–5, filtrate after 1, 2, 3, 4, and 6 hr of reaction, respectively; 6, solution of bisphenols mixture.

The filtrate remaining after precipitation of the polymer was concentrated and analyzed by TLC on silica gel in a developing system of benzene–methyl alcohol (9:1 w/w). Chromatograms were developed by means of iodine vapors.

In the samples of copolyesters obtained from monomers of system I, the chlorine content was also determined (Table III).

The experimental data show that the composition of the copolycondensation product depends on the reactivity ratio of the monomers. At temperatures lower than the isokinetic one (180°C), phenolphthaleine ($k = 0.64 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$) is more reactive than dichlorobisphenol A ($k = 0.56 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$), and in the initial stage of the copolycondensation reaction, macromolecules therefore contain more monomer units of phenolphthaleine and terephthaloyl chloride. At the isokinetic temperature (242°C), the reactivity of both monomers should be equal. The investigations proved that at this temperature the copolyester composition does not depend on the extent of reaction and equals the composition of the initial mixture at the start of the reaction.

The rate of disappearance of monomers from the reaction mixture was observed on chromatographs of filtrates obtained after isolating the polymer from the samples that were taken during the copolycondensation process. Figures 4 and 5 present chromatograms for the copolyester filtrates from phenolphthaleine, dichlorobisphenol A, and terephthaloyl chloride. These chro-

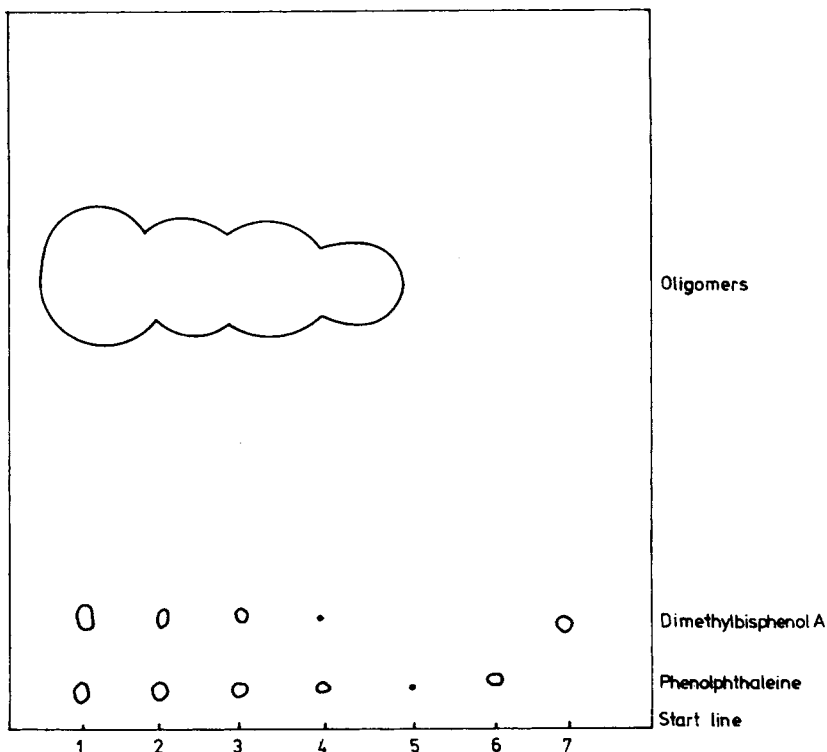


Fig. 7. Analysis of filtrates of copolyester samples obtained from terephthaloyl chloride, phenolphthaleine, and dimethylbisphenol A at 220°C ($T > T_i$): 1–5, filtrate after 60, 90, 120, 210, and 300 min of reaction, respectively; 6, solution of phenolphthaleine; 7, solution of dimethylbisphenol A.

matograms show that at the isokinetic temperature, monomers vanish from the reaction medium at an equal rate and, when the temperature is lower than isokinetic one, the monomer that is more active at this temperature (i.e., phenolphthaleine) disappears more quickly.

Chromatograms of the oligomeric part of the copolyester from system II, i.e., phenolphthaleine, dimethylbisphenol A, and terephthaloyl chloride (Figs. 6–8), also show the character of the changes in composition that accompany the changes in temperature and extent of the reaction. At temperatures lower than the isokinetic one (180°C), phenolphthaleine, which is more reactive at these temperatures ($k = 0.64 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$), vanishes more quickly from the reaction medium than dimethylbisphenol A ($k = 0.49 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$); however, at temperatures higher than the isokinetic one (220°C), phenolphthaleine is less reactive ($k = 2.50 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$), and dimethylbisphenol A ($k = 4.10 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$) disappears sooner. At the isokinetic temperature (200°C), both monomers disappear simultaneously.

The results of our investigations show that the composition of the product of high-temperature copolycondensation carried out in a solution depends on the reactivity of the monomers with the intermonomer. An additional dependence on the extent of reaction was also observed.

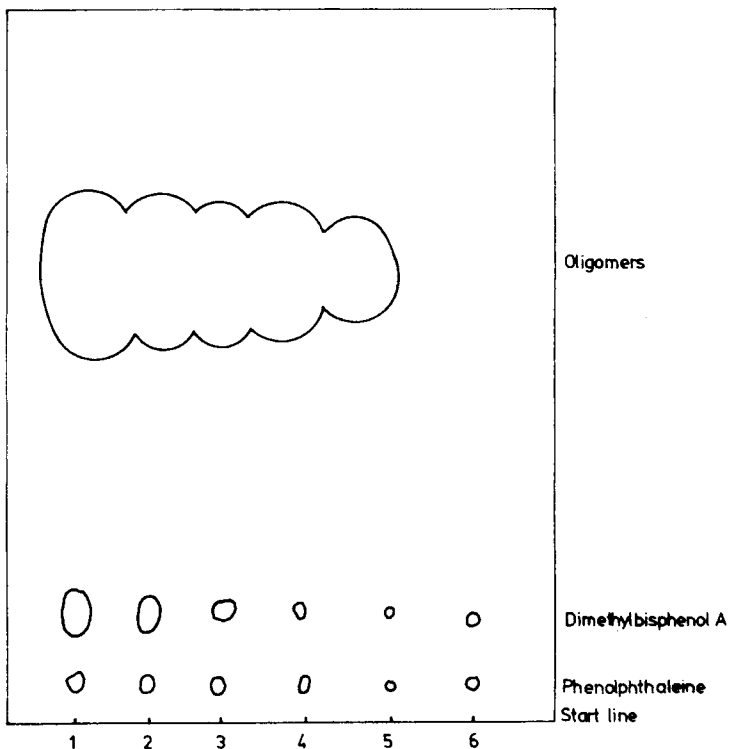


Fig. 8. Analysis of filtrates of copolyester samples obtained from terephthaloyl chloride, phenolphthaleine, and dimethylbisphenol A at 200°C ($T = T_i$): filtrate after $\frac{1}{2}$, 1, $1\frac{1}{2}$, 3, and 6 hr of reaction, respectively; 6, solution of bisphenols mixture.

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