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Novel Rearrangement in the Synthesis of Poly(phthalidylidenearylene)s by Self-Condensation of 3-Aryl-3-chlorophthalides. 2. Effect of Monomer Structure and Reaction Conditions

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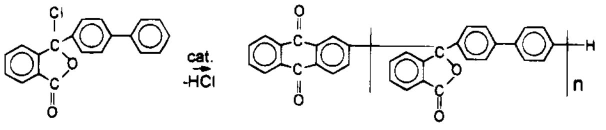
ABSTRACT: The Friedel−Crafts self-condensation of 3-aryl-3-chlorophthalides monosubstituted in the phthalide ring has been studied. 3-Aryl-3-chlorophthalides containing Cl, Br, F, and NO_2 as substituents were polymerized in solutions of nitrobenzene and dichloroethane in the presence of Lewis acids as a catalyst. The structures of the polymers obtained were established by ^{13}C NMR spectroscopy. The monomers containing substituents at the 4- and 6-positions of the phthalide ring were found to partially rearrange in the course of the polymer synthesis, giving rise to isomeric units in the polymer. From the effect of reaction conditions on the monomer rearrangement a mechanism has been proposed.

Introduction

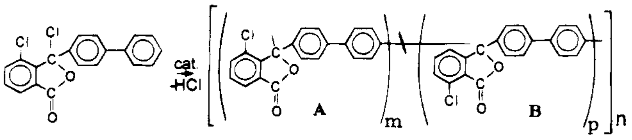
Recently, a large variety of high-temperature, solvent-resistant polymers of the poly(phthalidylidenearylene) class has been synthesized.[1−9] These polymers are obtained by electrophilic polycondensation reactions of bis(pseudochloroanhydrides) of aromatic diketo acids [bis(3-aryl-3-chlorophthalides)] with aromatic hydrocarbons or by self-condensation of pseudochloroanhydrides of aromatic keto acids (3-aryl-3-chlorophthalides).

Under optimal conditions, the polycondensations proceed with high regioselectivity, yielding polymers with para-substituted aromatic fragments in the main chain. For example, self-condensation of 3-(4-biphenylyl)-3-chlorophthalide (**1**) results in high molecular weight poly(3,3-phthalidylidene-4,4′-biphenylylene) (**2**):



1 **2**

It seems reasonable to assume that self-condensation of **1a**, containing unreactive substituents on the phthalide ring, would give rise to a polymer with substituents in the same positions of the phthalide ring. However, quite unexpectedly, we discovered that introduction of chlorine into the 4-position of the phthalide ring yields polymer **2a** with two types (A and B) of repeating units:[8,9]



1a **2a**

The structural assignment of **2a** was based on the analysis of ^{13}C NMR spectra of both polymers and model compounds. The polymers were obtained in near quantitative yield. The intrinsic viscosity of the polymers (in 1,1,2,2-tetrachloroethane) reached as high as 1.52 dL/g. The ratio of isomeric units (A and B) in such polymers was ca. 1:1.

To the best of our knowledge, rearrangement of this kind has not been reported either for monomers like 3-aryl-3-chlorophthalides or Friedel−Crafts polymerizations.

The aim of this paper is to examine the influence of variables affecting the rearrangement processes. These include the effects of monomer structure and concentration, type and amount of catalyst, reaction temperature, and solvent on the self-condensation of 3-aryl-3-chlorophthalides.

Experimental Section

Synthesis of Monomers. 3-Aryl-3-chlorophthalides were synthesized in two stages. In the first stage, aromatic hydrocarbons were acylated by substituted phthalic anhydrides in the presence of aluminum chloride ($AlCl_3$) according to a technique described elsewhere.[10] The resulting ortho-keto acids were treated by thionyl chloride ($SOCl_2$) followed by recrystallization of the 3-aryl-3-chlorophthalides formed from a $SOCl_2$−hexane mixture, as described in ref 11. Their melting points are presented in Table 1. Monomers **1h**−**1j** were obtained as isomer mixtures and used without separation. The structure of these monomers was confirmed by ^{13}C NMR spectroscopy. The assignments of carbon chemical shifts for the monomers are given in Table 2.

Polycondensations. The polymers were synthesized by self-condensation of 3-aryl-3-chlorophthalides according to a known method.[7−9] A typical procedure of polymer synthesis was as follows. A 100 mL flask with reflux condenser was charged under an argon atmosphere with **1a** (3.54 g, 10 mmol) and nitrobenzene (5 mL). The resultant mixture was heated to 100 °C, and $SbCl_5$ (1.28 mL, 1 mmol) was added. The solution was stirred for 10 h at 100 °C and was then cooled, diluted with chloroform, and poured into methanol. The polymer precipitated was filtered off and washed with methanol and acetone. Then it was dried at 120 °C for 8 h. Yield after drying: 3.08 g (97%), intrinsic viscosity $[\eta]_{TCE} = 1.52$ dL/g.

Measurements. ^{13}C NMR spectra of monomers and polymers were recorded on JEOL FX-90Q and Bruker AMX-600

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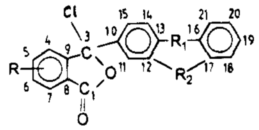
Table 1. Monomer Structure and Characterization



sample	R_1	R_2	R	mp (°C)[a]
1a		No	4-Cl	110–111
1b		CH_2	4-Cl	159.5–161
1c	O	No	4-Cl	112–113.5
1d		No	4-F	130–131.5
1e		No	5-NO_2	146–147.5
1f		No	6-NO_2	175–176
1g		No	5-Br	130–135
1h[b]		No	6-Br	
1i[b]		No	5-Cl	
1j[b]		No	6-Cl	

[a] Mp values were determined at heating rate of 4 °C/min. [b] Nonisolated isomers.

spectrometers operating in the pulsed FT modes, at 22.5 and 150.94 MHz (for ^{13}C frequencies), using tetramethylsilane (TMS) as an internal standard and reported in ppm. The deuterated solvents used for preparation of monomer and polymer solutions are given in Tables 2 and 3, respectively. The viscosity of polymer solutions in 1,1,2,2-tetrachloroethane was measured at 25 °C in a viscosimeter of the Ubbelohde type. The intrinsic viscosity was calculated by extrapolating reduced viscosity to zero concentration. Melting points were determined with a homemade melting point determinator, at heating rate 4 °C/min.

Results and Discussion

A possible mechanism for the formation of B-type units by self-condensation of **1a** has previously been proposed.[9]

In the present study the rearrangement scheme of the reactive end fragment of the growing macromolecular chain is presented in more detail (Figure 1).

As can be seen, the reactive end unit of the macromolecular chain in the presence of a Lewis acid catalyst (i.e. $AlCl_3$) generates cation **3** which undergoes ring-opening to produce cation **4**. After intramolecular ipso attack of the acyl ion on the aromatic ring, σ-complex **6** is obtained. The σ-complex may then form the open-chain cation **7**. After nucleophilic attack of the carbonyl oxygen on the electron deficient carbon of the acyl ion, ring closure and formation of isomeric cation **8** occur, the latter's involvement in the reaction giving rise to the elementary isostructure units **10**. It should be pointed out that intermediates **4**, **6**, and **7** may also form anthraquinone groups **5** and **9**.

It is clear that the intramolecular cyclization leading to quinone formation terminates chain growth. Quinone formation was found to be dominant among side reactions.[3] Because of intensive absorption in the UV- and IR-spectral regions, end quinone groups formed could even be used for determination of the number-average molecular weight of the polymer.[12]

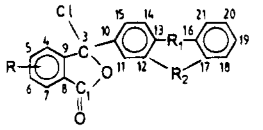
On the whole, the rearrangement suggested is a multistep process including both equilibrium and nonequilibrium steps. Within this context the following basic question arises: what is the driving force for such a rearrangement?

It seems very likely that the rearrangement proposed represents a consequence of cation transformations resulting in formation of more stable ions (e.g. **8**). From this point of view, analysis of the results of polymer preparations using different monomers and different reaction conditions may contribute to clarify the rearrangement mechanism.

The results obtained in the present investigation will be discussed as follows:

1. Effect of reaction conditions on the self-condensation of **1a**.
2. Effect of substituents on the aromatic nucleus of the phthalide ring on the self-condensation of **1a**–**1j**.

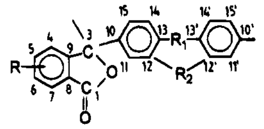
Table 2. Chemical Shifts (δ, ppm, TMS) and Multiplicity of Signals in ^{13}C NMR Spectra of Monomers 1a–1g



	samples						
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
C^1	165.52 s[a]	165.90 s	165.67 s	165.52 s	165.03 s	164.54 s	165.90 s
C^3	99.96 s	100.50 s	100.07 s	98.07 s	99.96 s	99.04 s	99.80 s
C^4	129.76 s	130.03 s	130.16 s	155.94 s (259 Hz)	119.74 d	124.78 d	128.62 d
C^5	136.48 d	136.59 d	136.82 d	122.78 d (20 Hz)	153.71 s	130.30 d	131.06 s
C^6	132.61 d	132.53 d	133.04 d	133.70 d (7 Hz)	127.48 d	149.70 s	135.29 d
C^7	124.29 d	124.40 d	124.67 d	122.07 d	128.43 d	121.63 d	127.91 d
C^8	126.54 s	126.90 s	126.90 s	121.91 s	129.60 s	125.15 s	123.26 s
C^9	146.48 s	147.04 s	146.68 s	136.80 s (15.9 Hz)	152.84 s	155.88 s	153.71 s
C^{10}	133.99 s	133.28 s	129.83 s	135.61 s	137.08 s	135.29 s	137.62 s
C^{11}	126.89 d	120.39 d	127.22 d	126.48 d (2.4 Hz)	127.95 d	126.24 d	127.11 d
C^{12}	127.22 d	143.74 s	117.89 d	127.27 d	128.24 d	128.18 d	127.76 d
C^{13}	142.71 s	143.36 s	159.34 s	143.04 s	143.96 s	143.52 d	143.74 s
C^{14}	127.22 d	125.70 d	117.89 d	127.27 d	128.24 d	128.18 d	127.76 d
C^{15}	126.89 d	127.54 d	127.22 d	126.48 d (2.4 Hz)	127.95 d	126.24 d	127.11 d
C^{16}	139.35 s	140.39 s	156.08 s	139.68 s	140.44 s	139.46 s	140.54 s
C^{17}	126.89 d	143.74 s	119.88 d	127.01 d	127.81 d	127.16 d	128.08 d
C^{18}	128.79 d	119.80 d	128.86 d	128.84 d	128.27 d	129.00 d	129.60 d
C^{19}	127.81 d	126.90 d	124.42 d	127.87 d	127.70 d	127.75 d	127.59 d
C^{20}	128.79 d	126.90 d	128.86 d	128.84 d	128.27 d	129.00 d	129.60 d
C^{21}	126.89 d	125.10 d	119.88 d	127.01 d	127.81 d	127.16 d	128.08 d
C^{22}		36.90 t					
solvent	$CDCl_3$	$CDCl_3$	CD_2Cl_2	$CDCl_3$	THF-d_8	$CDCl_3$	$CDCl_3$

[a] Key: s, singlet; d, doublet; t, triplet.

Table 3. Chemical Shifts (δ, ppm, TMS) and Multiplicity of Signals in ^{13}C NMR Spectra of Synthesized Poly(phthalidylidenearylene)s



	samples									
	2a^{a,b}	**2b**^{a}	**2c**	**2d**^{a,c,d}	**2e**	**2f**^{c}	**2g**^{d}	**2h**	**2i**	**2j**^{d}
C^1	168.88 s 166.88 s	168.66 s 166.60 s	168.28 s	168.16 s 165.47 s	167.24 s	167.09 s	168.45 s	167.85 s	168.33 s	168.04 s
C^3	92.90 s 90.28 s	93.51 s 90.85 s	92.16 s	90.98 s 90.98 s	91.71 s	91.83 s	90.81 s	91.24 s	90.83 s	91.27 s
C^4	130.88 s 123.09 d	130.52 s 122.86 d	130.30 s	156.82 s 120.26 d	120.70 d	127.54 d		125.70 d	125.34 d	
C^5	136.49 d 135.62 d	136.12 d 135.12 d	135.94 d	122.00 d 136.85 d	153.46 s	129.54 d	129.60 s	137.40 d	141.06 s	134.69 d
C^6	131.98 d 131.37 d	131.45 d 130.87 d	131.44 d	132.41 d 116.60 d	128.12 d	157.28 s	133.23 d	123.64 s	133.55 d	135.99 s
C^7	125.37 d 134.10 s	124.99 d 133.68 d	125.74 d	122.42 d 159.80 s	125.99 d	121.74 d	125.64 d	129.06 d	126.10 d	125.83 d
C^8	129.07 s 122.58 s	128.77 s 122.28 s	128.52 s	128.80 s 113.60 s	131.07 s	127.87 s	124.45 s	127.50 s	124.02 s	127.38 d
C^9	148.54 s 154.43 s	148.65 s 154.50 s	148.18 s	137.78 s 153.35 s	153.07 s	150.13 s	153.33 s	150.35 s	153.90 s	149.91 s
C^{10}, $C^{10'}$	137.12 s 140.10 s	136.55 s 139.61 s	132.42 s	138.61 s 139.71 s	140.54 s	140.28 s	139.46 s	139.46 s	139.51 s	139.62 s
C^{11}, $C^{11'}$	129.76 d 128.11 d	119.78 d 120.24 s	130.41 d	128.01 d 127.26 d	128.50 d	128.38 d	127.54 d	127.54 d	127.62 d	127.62 d
C^{12}, $C^{12'}$	127.27 d 127.75 d	143.64 s 144.16 s	118.38 d	127.26 d	128.11 d	128.08 d	127.32 d	127.32 d	127.38 d	127.38 d
C^{13}, $C^{13'}$	141.12 s 141.12 s	141.64 s 141.55 s	157.13 s	140.86 s 140.78 s	141.58 s	141.35 s	140.60 s	140.60 s	140.65 s	140.65 s
C^{14}, $C^{14'}$	127.27 d 127.75 d	127.91 d 126.22 d	118.38 d	127.26 d	128.11 d	128.08 d	127.32 d	127.32 d	127.38 d	127.38 d
C^{15}, $C^{15'}$	129.76 d 128.11 d	125.51 d 123.94 d	130.41 d	128.01 d	128.50 d	128.38 d	127.54 d	127.54 d	127.62 d	127.62 d
$-CH_2-$		37.7 t								
solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	THF-d_8	THF-d_8	$CDCl_3$		$CDCl_3$	

[a] The first and second values for each carbon signal are assigned to units A and to isounits B, respectively. [b] Recorded at 150.9 MHz. [c] J_{C_i-F} values are not given because they are similar to those obtained for monomer **1d** (cf. Table 2). [d] The signals of some carbon atoms were not identified due to broadening and/or coincidence of signals.

3. Effect of the aryl substituent on the rearrangement of the monomers **1b** and **1c**.

4. Chain structural aspects.

1. Effect of Reaction Conditions on the Self-Condensation of 1a. Chlorinated aliphatic solvents (dichloroethane, methylene chloride) and nitrobenzene were used for the polymer synthesis. Chlorinated aliphatic solvents were found to be unsuitable solvents for substituted 3-aryl-3-chlorophthalides (especially those containing substituents such as a nitro- group). Polycondensations in chlorinated solvents in some cases proceed in a heterogeneous reaction medium, yielding low molecular weight polymers. Nitrobenzene turned out to be more convenient for self-condensations of substituted 3-aryl-3-chlorophthalides, affording high molecular weight polymers.

Self-condensations of **1a** were conducted at variable temperature and monomer and catalyst concentrations (Table 4). The yield of the polymers was close to quantitative. The assignments of carbon chemical shifts for the polymers synthesized are given in Table 3.

As can be seen, an increase of the reaction temperature from 80 to 100 °C results in an increase of both polymer viscosity and the amount of rearranged units. Higher temperature causes a significant increase in the content of B units. However, because of intensive quinone-forming side reactions, the polymer viscosity decreases dramatically.

These findings can be explained in the following way. At the higher temperature the equilibrium favors the open chain ion **4**, which may either cyclize to the quinone structure **5** or may transform to intermediate **7**. There is also the possibility of transformation of ion **7** into **9**. Very likely, all these processes take place. It is also true that if there had not been a quinone-forming side reaction, the polymer would have a much higher molecular weight.

It is common knowledge that in a polycondensation reaction the properties of the polymer produced are significantly influenced by monomer concentration. This is particularly the case for polymer synthesis in which concurrent intramolecular reactions can occur. Indeed, a decrease of monomer concentration favors such intramolecular reactions as quinone formation and rearrangement. However, the polymer viscosity is concurrently decreased.

On the whole, the above results are in accordance with the rearrangement scheme proposed. However, as far as catalyst is concerned, the interpretation of catalyst effect on the rearrangement is not unambiguous.

First of all, the A:B isomer ratio does not depend on the catalyst type (Table 4). Under similar conditions, the same A:B isomer ratio is observed for all the catalysts. Moreover, the A:B ratio does not depend on the amount of the catalyst. At present, it is difficult to explain these results. Apparently, the catalyst is mostly

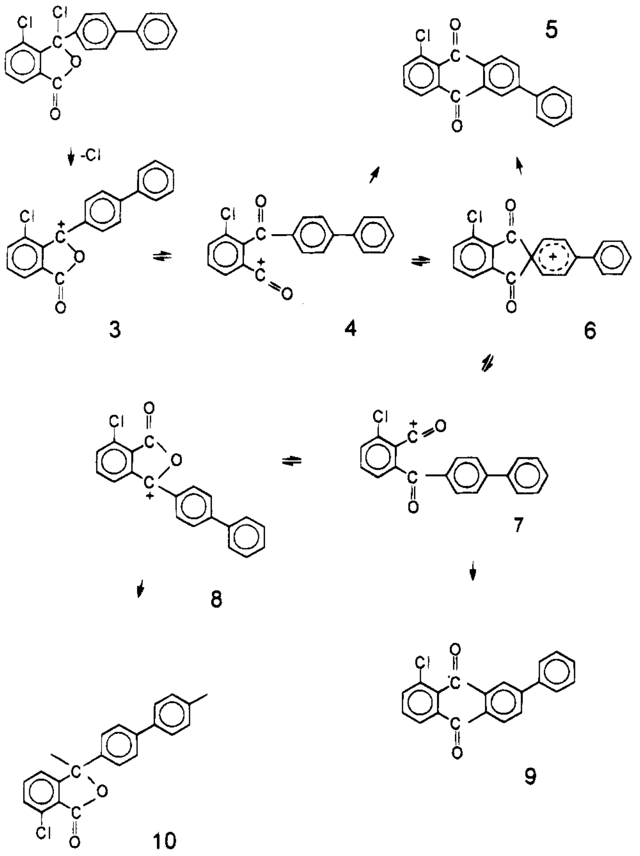


Figure 1. Rearrangement scheme.

Table 4. Effect of Reaction Conditions on the Self-Condensation of Monomer 1a[a] and Variation of Intrinsic Viscosity, [η], and Isomer Unit Ratio, A:B, for Polymer 2a

catalyst	[catalyst]/[monomer]	monomer concn (mol/L)	reacn temp (°C)	[η][b] (dL/g)	A:B[c]
$SbCl_5$	0.10	2	80	1.02	3:2
$SbCl_5$	0.10	2	100	1.52	1:1
$SbCl_5$	0.10	2	170	0.48	1:4
$SbCl_5$	0.10	1	100	0.72	3:4
$SbCl_5$	0.10	0.5	100	0.50	3:5
$InCl_3$	0.05	2	100	0.88	1:1
$InCl_3$	0.10	2	100	1.12	1:1
$AlCl_3$	1.4	2	100	0.92	1:1

[a] Conditions: solvent, nitrobenzene, reaction time, 10 h; polymer yield, close to quantitative in all cases. [b] Measured at 25 °C in 1,1,2,2-tetrachloroethane. [c] From NMR data.

involved in the first step of the reaction. Additional experiments and theoretical calculations are needed to clarify the effect of the catalyst and counterion on the rearrangement.

2. Effect of Substituents on the Aromatic Nucleus of the Phthalide Ring on the Self-Condensation of 1a−1j. If the rearrangement represents the consequence of cation transformations, the type and positions of substituents on the aromatic nucleus of the phthalide moiety should affect the process strongly.

Table 5. Isomer Unit Ratio, A:B, in Self-Condensation of Monomers 1a−1j

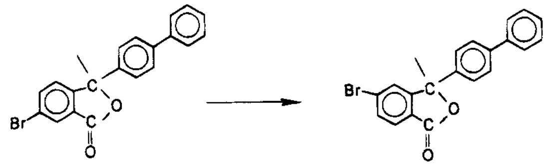
monomer	R	A:B
1a	4-Cl	1:1
1d	4-F	4:1
1e	5-NO_2	1:0
1f	6-NO_2	1:0
1g	5-Br	1:0
1g + **1h**	5-Br + 6-Br	*a*
1i + **1j**	5-Cl + 6-Cl	*b*
1b	4-Cl	3:1
1c	4-Cl	1:0

[a] Observed increased content of 5-Br units due to rearrangement of 6-Br units into 5-Br ones. [b] The ratio of isomer units in the polymer was similar to that of the initial monomer mixture.

All the self-polycondensations of monomers **1a**−**1g** were conducted under the same conditions. The A:B isomer ratio of the polymers obtained was also estimated by NMR spectroscopy. It is clear from the data presented in Table 5, that chlorine at the 4-position of the aromatic nucleus reveals a stronger influence on the rearrangement than does fluorine. Furthermore, self-condensation of monomers **1e**−**1g** led to polymers with A-type units only. Therefore, a nitro group at the 5- or 6-position as well as bromine at the 5-position did not produce any rearrangement.

Because our attempts to separate monomer mixtures **1g** + **1h** and **1i** + **1j** failed, we used the monomer mixtures for polymer synthesis. As shown above, a higher reaction temperature results in an increased amount of the rearranged units. Therefore, comparison of the results of two polycondensations conducted with the same monomer mixture, but at two different temperatures, should allow identification of the monomer which undergoes rearrangement.

Thus, analysis of NMR spectra of polymers obtained by self-polycondensation of the **1g** + **1h** mixture at 85 and 110 °C has shown that the polymer obtained at 110 °C was enriched for bromine in the 5-position. One can show that according to the scheme proposed the rearrangement of the 6-brominephthalide monomer results in the 5-bromine monomer:



Therefore, the 6-brominephthalide monomer undergoes rearrangement, while the 5-positioned bromine monomer does not rearrange.

The idea of using the temperature effect to enhance the rearrangement was checked by experiment with monomers **1e** and **1f**. The monomers were found not to rearrange. Therefore, polycondensations conducted with the same mixture of these monomers at two different temperatures should reveal no differences in their content of isomeric units. Indeed, spectral analysis has shown a similar isomeric unit ratio for polymers obtained at different temperatures.

The monomer mixtures of **1i** + **1j** were similarly subjected to polycondensations at different temperatures. The spectra of the polymers obtained were quite similar. Therefore, monomers with chlorine in the 5- and 6-positions do not rearrange under the used conditions.

It is, therefore, clearly established that chlorine at the 4-position and bromine at the 6-position exert the greatest effect on the rearrangement, while a chlorine and nitro group at the 5- and 6-positions and bromine at the 5-position exert no effect.

It should be noted that the present conclusions are necessarily relevant only for the monomers involved in

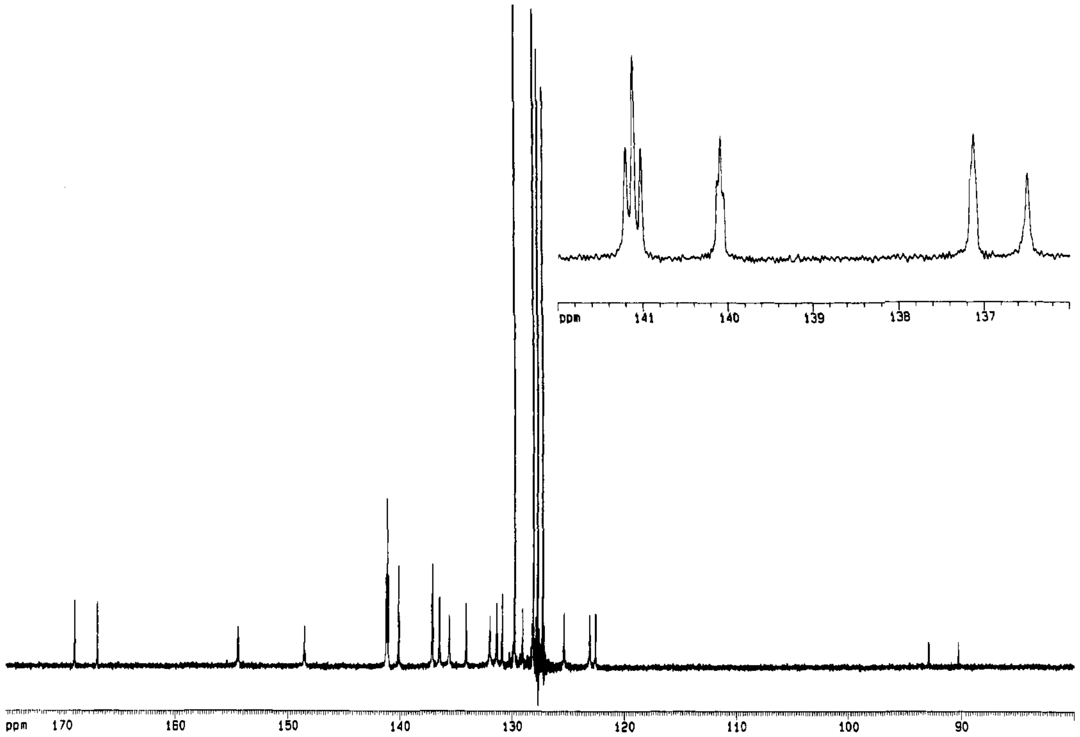


Figure 2. ^{13}C NMR spectrum of a $CDCl_3$ solution of **2a** recorded at 150.9 MHz.

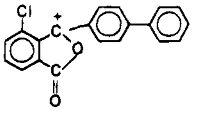
the polycondensations carried out under the conditions stated here.

3. Effect of the Aryl Substituent on the Rearrangement of Monomers 1b and 1c. We have previously reported[1] that self-condensation of 3-aryl-3-chlorophthalides containing fluorene and diphenyl ether as their moieties proceed readily to give higher molecular weight polymers. The finding is in good agreement with the high reactivity of fluorene and diphenyl ether in electrophilic substitution reactions. Further, it is well-known that the rate of electrophilic acylation of diphenyl ether is greater than that of fluorene and much greater than that of biphenyl. Maybe owing to the higher reactivity of diphenyl ether, self-condensation of 3-(4-phenoxyphenyl)-3-chlorophthalide affords high molecular weight polymers in the presence of a very small amount of catalyst. It is noteworthy that obtained polymers contain practically no anthraquinone groups. In contrast, self-condensation of 3-(2-fluorenyl)-3-chlorophthalide is accompanied by formation of a significant amount of quinone groups (in comparison, e.g., with the self-condensation of **1**).

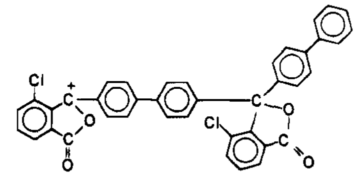
Self-condensations of **1b** and **1c** were found to give high molecular weight polymers as well. However, monomer **1b** undergoes rearrangement to a smaller extent that **1a**, while monomer **1d** does not rearrange at all. The latter result can be explained by the high stability of ion **3**. As a consequence, there is no quinone-forming side reaction, nor any open-chain cation transformation resulting in iso-units. Therefore, the highly electron donating effect of aryl substituents prevents rearrangement.

In addition, the electron donating effect of the aryl substituent can reveal itself in two alternate ways, i.e. by the effect of unreacted (monosubstituted) aryl substituent on one hand or by the effect of the reacted (disubstituted) aryl substituent on the other.

Thus, in the self-condensation of **1a** the situation is illustrated by structures **11** and **12**, respectively:



11



12

Clearly, the effect of these substituents is quite different. In comparison with **11**, the electron donating effect of biphenyl in **12** is reduced due to presence of a second phthalidyl substituent. On the other hand, the phthalidyl substituent (and the next biphenyl fragment) may form a conjugated system. It is worthy to note that attempts to obtain rearranged diaryl phthalide by condensation of **1a** with an excess of biphenyl (a biphenyl excess was used to suppress the polymer-forming reaction) failed. Indeed, 3,3-bis(biphenylyl)-phthalide has been obtained in quantitative yield. Therefore, the **11** does not rearrange. Obviously, a structure like **12** plays a major role in the rearrangement. Above all, it is well-known that monomers in polycondensations react at the very beginning of the synthesis to give dimers, trimers, etc. Further chain growth is due to reactions of the oligomers. It is remarkable that even low molecular weight oligomers were found to consist of two isomer structures in approximately equal ratios. Moreover, the isomer unit ratio does not depend on the reaction time and, consequently, on the chain length. Probably, the rearrangement starts from dimers or trimers, which may stabilize intermediate σ-complexes. It is very likely that the stabilization of the σ-complex is the main reason for the monomer rearrangement during polycondensation. This effect should be taken into account in studies aimed to get a complete stoichiometric monomer rearrangement during polycondensation.

With respect to similar monomer rearrangements Hayashi, in 1927, was the first to report[13] the occurrence of a sulfuric acid catalyzed molecular rearrangement in the course of ring closure of certain substituted *o*-benzoylbenzoic acids. Later, several instances of this remarkable rearrangement were recorded and the mechanism elaborated in some detail.[14-16] Despite particular differences, e.g. the direction of carbenium center transfer in Hayashi's rearrangement is determined by sulfuric acid concentration and reaction temperature, catalysts such as trifluoroacetic acid, methanesulfonic acid, and poly(phosphoric acid) were shown to be unsuitable acidic catalysts. The rearrangement of both pseudochloroanhydrides and ortho-keto acids can be presumed essential for the process of generation and transfer of carbenium centers in ortho-keto carbonic acids and their derivatives. It may be presumed that similar processes would occur in their heteroatom-containing analogues.

4. Chain Structural Aspects. It was reported recently[9] that the ^{13}C NMR spectrum of **2a** in solution taken ion a JEOL FX-90Q spectrometer working at 22.5 MHz consisted of two sets of signals corresponding to A and B isomer units, exclusively. This most probably indicates the presence of two homopolymers **13**, or the presence of copolymers and block copolymers with sufficiently long blocks **14**, or the coexistence of the structures **13** and **14**, or strictly alternating copolymer **15**:

-A-A-A-A-A-A-A-A-
-B-B-B-B-B-B-B-B- **13**
-A-A-A-A-A-A-B-B-B-B-B- **14**
-B-A-B-A-B-A-B-A-B-A-B- **15**

In order to obtain more evidence about the chain structure of this polymer, we have recorded the corresponding ^{13}C NMR spectra on a higher field NMR spectrometer operating at 150.9 MHz. The spectrum of **2a** is shown in Figure 2. At first sight, the spectrum is very similar to that obtained previously. However, a careful analysis showed the presence of a higher number of ^{13}C-decoupled resonances than expected for the polymer which could adopt one of the above mentioned structures. At least five signals corresponding to $C^{13}_{A,B}$, C^{10}_{B}, C^{10}_{A}, $C^{12,14}_{A}$, and $C^{12,14}_{B}$, centered at 141.12, 140.10, 137.13, 127.75, and 127.27 ppm, respectively, appeared split as a set of signals of different intensities. Three of them ($C^{13}_{A,B}$, C^{10}_{B}, and C^{10}_{A}) are shown in the expanded region represented in Figure 2 (top). The presence of these "new" resonances is a direct indication of a different microstructure composition, more typical for random copolymers. The idea is in good agreement with conclusions which can be drawn from common knowledge about the preparation of aromatic polymers via electrophilic aromatic substitution reactions.

Conclusions

In this work, Friedel–Crafts electrophilic self-condensation of different monomers of 3-aryl-3-chlorophthalides was carried out and polymers containing isomer (rearranged) units were obtained. Different effects of phthalide substituents on the molecular rearrangement were observed. Chlorine and fluorine at the 4-position and bromine at the 6-position exert the greatest effect on the rearrangement, while chlorine and a nitro group at the 5- and 6-positions and bromine at the 5-position exert no effect. The reaction conditions were found to affect the rearrangement. ^{13}C NMR spectroscopic studies of the polymers containing rearranged units suggest that the materials are random copolymers.

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