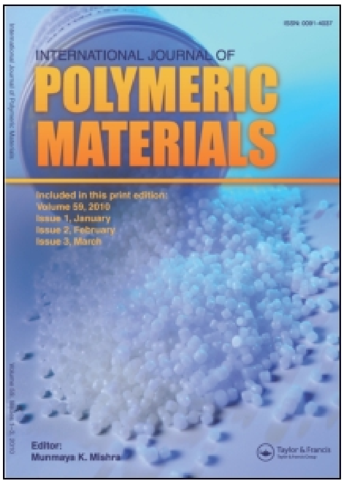

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Branching and Curing in the High Temperature Synthesis of Polymers Containing α-Diketone Groups

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Branching and Curing in the High Temperature Synthesis of Polymers Containing α-Diketone Groups

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The mechanism of polyether-α-diketones formation under nucleophilic substitution conditions are investigated using as example the reaction between 4,4'-difluorobenzyl (4,4'-DFB) at 160–180°C. The reactions are carried out in presence of K_2CO_3 in dimethylacetamide (DMAA) and chlorobenzene or toluene.

KEY WORDS α-Diketone polymers, synthesis, high temperature, branching, curing, reaction mechanisms.

Aromatic polyetherketones possess many valuable properties and have broad technical application.[1,2] One of the main methods of polyetherketones synthesis is known to be the nucleophilic substitution reaction of activated dihalogen aromatic derivatives. Therefore it seemed to be interesting also to introduce an α-diketone groups into the corresponding dihalogen aromatic compound that could make halogen atoms more reactive in such reactions.[3,4]

It also offers new opportunities to further improvement of their properties due to subsequent chemical conversions, mainly preparation of linear, branched, and network polymers having higher heat resistance.

In this paper regularities of polyether-α-diketones formation (under nucleophilic substitution conditions) are investigated on the example of reaction between 4,4'-difluorobenzyl (4,4'-DFB) and bisphenol A at 160–180°C in the presence of K_2CO_3 in dimethylacetamide (DMAA) and chlorobenzene (or toluene) medium (in 1.0:1.0 ratio):

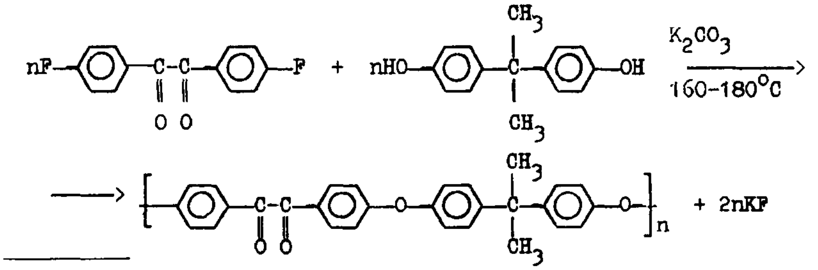

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TABLE I

Influence of the reaction conditions on the polycondensation of 4,4-diflurobenzyl (4,4'-DFB) with bisphenol A in DMAA and toluene mixture in the presence of K_2CO_3

	Reaction conditions[1]				Polymer					
	Excess[2]						Solubility			
Exp. No.	4,4'-DFB mol. %	K_2CO_3 wt. %	Temp. °C	Time, h	Method of adding	η_{inh}[3] (NMP) dL/g	THF	CHL.	TCE	NMP
1	0	40	180	5	Simultaneous	—	ins	ins	ins	ins
2	0	40	180	8	Simultaneous	—	ins	ins	ins	ins
3	0	100	180	4	Simultaneous	—	ins	ins	ins	ins
4	5	40	180	5	Simultaneous	0.37[4]	ins	ins	s[5]	s[5]
5	5	40	180	10	Simultaneous	0.37[4]	ins	ins	s[5]	s[5]
6	5	40	180	5	Simultaneous	0.48[6]	s	s	s	s
7	5	40	160	8	Simultaneous	0.23	s	s	s	s
8	10	40	160	10	Simultaneous	0.27[7]	s	s	s	s
9	2.5	40	180	2	Subsequent[8]	0.53	ins	s[9]	ins	s[9]
10	0	40	180	3	Subsequent	0.44	ins	ins	ins	s[9]
11	0	0	180	3	Subsequent	0.30	s	s	s	s

[1] Reagent concentration in DMAA is 20–25 wt. % (it is slightly changed during reaction due to partially solvent evaporation at 180°C).

[2] Calculated per 1 mole of bisphenol A.

[3] For 0.5% solution in NMP at 25.0°C.

[4] A small quantity of gel is separated before viscosity measurement.

[5] Soluble upon heating.

[6] $\bar{M}_w$ = 45000 (by GPC with polyetherketone as standard).

[7] $\bar{M}_w$ = 35000 (by GPC with polyetherketone as standard).

[8] 4,4'-DFB is added into reaction mixture after completion of phenolate formation.

[9] Soluble after prolonged mixing at 20°C.

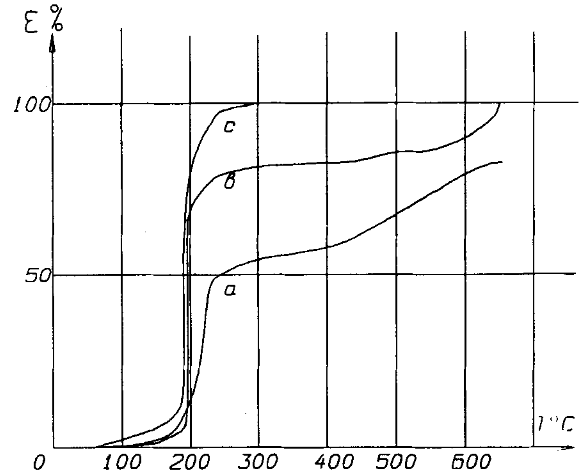


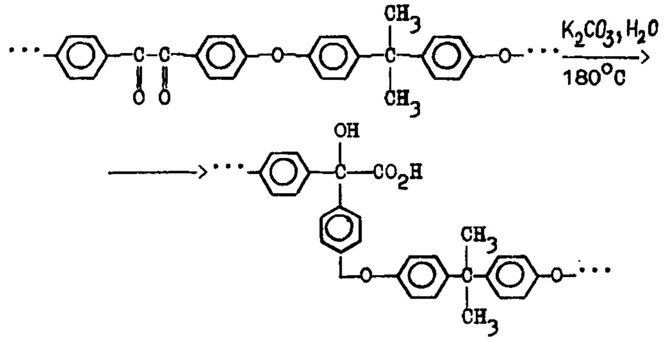
FIGURE 1 Thermomechanical curves of polyether-α-diketones based on 4,4′-difluorobenzyl and bisphenol A at different molar ratio: a) 1:1 and 100 wt % excess of K_2CO_3 (Table I, N 2); b) 1.05:1 and 40 wt % excess of K_2CO_3 (Table I, N 3); and c) 1:1 without excess of K_2CO_3 (Table I, N 7).

Because of its limited solubility and reactivity, potassium carbonate can be used in excess (30–100 wt%).

For high molecular weight polymer preparation the influence of various parameters such as monomer ratio, quantity of K_2CO_3, order of reagent addition, temperature and time on the polymer structure were investigated. The results are presented in Table I. It is shown that by simultaneous addition of all the reaction components, a stoichiometric monomer ratio and an excess of K_2CO_3 (40–100%) insoluble, probably network polymers are formed (Table I, NN 1–3) and their deformation upon compression does not reach 100% even at very high temperatures (Figure 1, a).

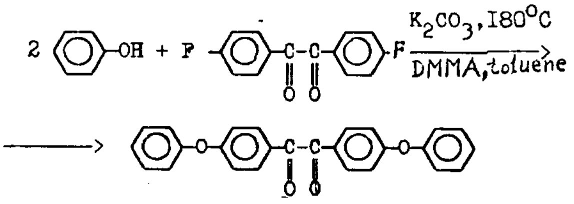
This may be due to the fact that the K_2CO_2 excess in the presence of water, leads to a benzyl rearrangement of —CO—CO— linkage.

Such reaction proceeded effectively at high temperature as shown in the following scheme:



Curing of polymers in such a case can be carried out by intermolecular reactions OH— and COOH— groups.

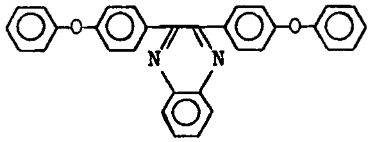
This supposition is confirmed by the behaviour of a model ether-α-diketone under such conditions:



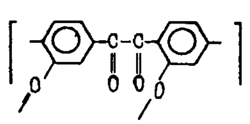
This diketone was treated with a 40% excess of K_2CO_3 in a medium of DMAA at 180°C for a few hours.

GPC investigation showed the occurrence of additional peaks in the chromatogram testifying to formation of compounds of both the higher (in quantity of 9–10%) and lower molecular weight (approx. 1%). In addition the chromatograms produced under adsorption conditions have an additional peak, testifying to formation of more polar groups, possibly OH-groups (Figure 2).

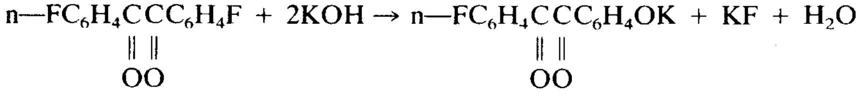
The correctness of the supposition concerning the possibility of a benzyl rearrangement was also confirmed by the following: the analogous etherquinoxaline obtained by the reaction of a quinoxaline containing monomer based on 4,4'-DFB and phenol is stable under such conditions (from GPC data) see Figure 2b:



The other reason for polymer branching and crosslinking during the high temperature synthesis of polyether-α-diketones can be the abstraction of ortho hydrogen atoms as for halogen or other activating groups which was known earlier for polyetherketones.[5]



Besides the benzyl rearrangement of 4,4'-DFB the reactivity can be changed because of a hydrolysis side reaction:



$$n\text{—}FC_6H_4\underset{O}{\underset{\|}{C}}\underset{O}{\underset{\|}{C}}C_6H_4F + 2KOH \rightarrow n\text{—}FC_6H_4\underset{O}{\underset{\|}{C}}\underset{O}{\underset{\|}{C}}C_6H_4OK + KF + H_2O$$

Because of the high volatility of 4,4'-DFB it can be readily evaporated from the reaction medium, influencing the stoichiometric ratio and leading to the termination of chain propagation. Taking into account the possible expenditure of 4,4'-DFB on such side reactions the investigation of the influence of this monomer excess on the molecular weight and structure of the polymer being formed was also carried out.

It was established that in the presence of a 5 mol % excess of 4,4'-DFB polymers

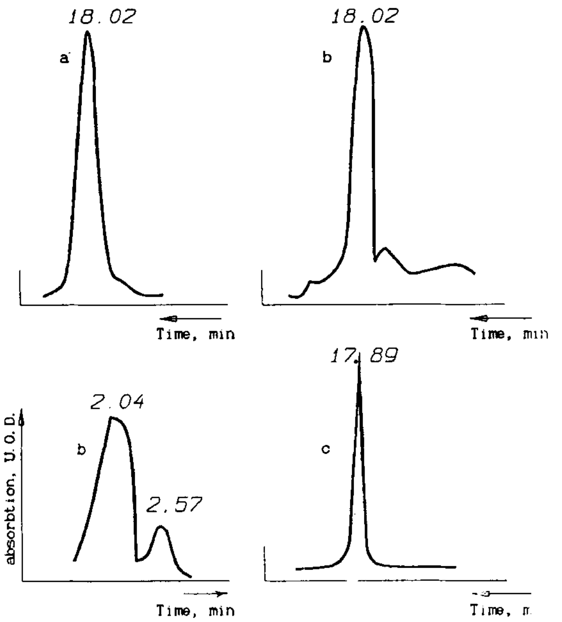


FIGURE 2 GPC chromatograms of ether-α-diketone: a) initial; b) treated by K_2CO_3 in the DMAA at 180°C; and c) etherquinoxaline based on ether-α-diketone (treated).

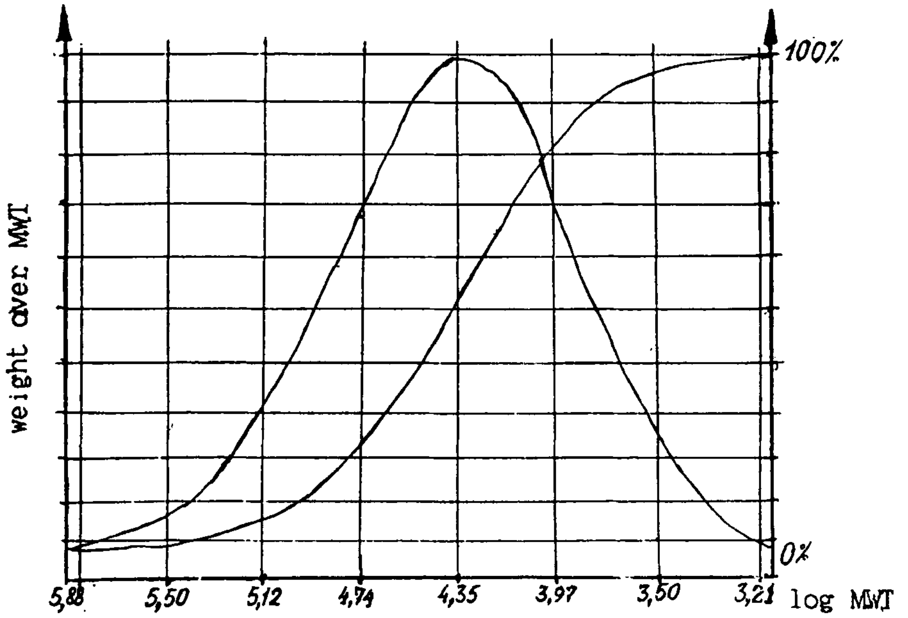


FIGURE 3 Molecular weight distribution curve of polyether-α-diketone based on 4,4'-DFB and bisphenol A taking in molar ratio 1.05:1.00 in the presence of 40 wt % K_2CO_3 excess.

containing an insignificant quantity of gel are formed (see Table I, NN 4.5 and Figure 1, comp. cur. b and c).

From the molecular weight distribution (MWD) curves (Figure 3) the soluble polymer fraction is characterized by definite branching (polydispersity index is 2.5–4.5). When the reaction time is decreased and under other similar conditions, highly soluble polymer was obtained—Table I, N 6 (the gel formation is not observed).

However according to the GPC data small quantities of microgel particles (≈7.4%) are present in this polymer (Figure 4a). A study of influence of reaction time on polymer molecular weight has shown that the reaction is completed at 180°C in 1.5 hours (Figure 5).

It was revealed that on reducing the reaction temperature to 160°C the polymers formed are highly soluble in THF or chloroform (Table I, NN 7.8) but they have lower inherent viscosity.

The absence of gel is also confirmed by the GPC data (see Figure 5b).

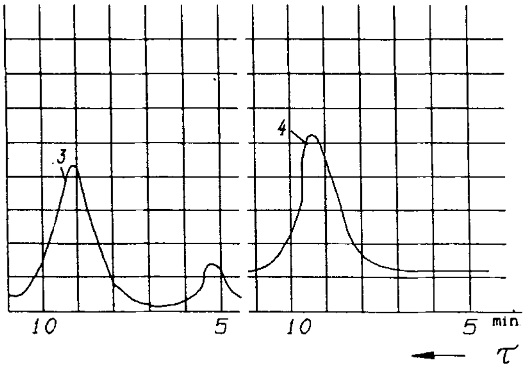


FIGURE 4 GPC-chromatograms of polyether-α-diketones based on 4,4′-DFB and bisphenol A (numbers of curves correspond numbers of polymers in Table I).

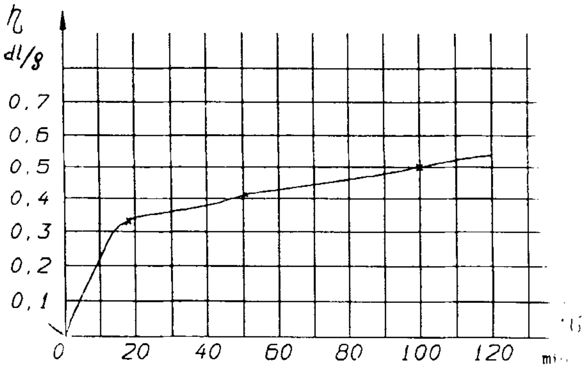
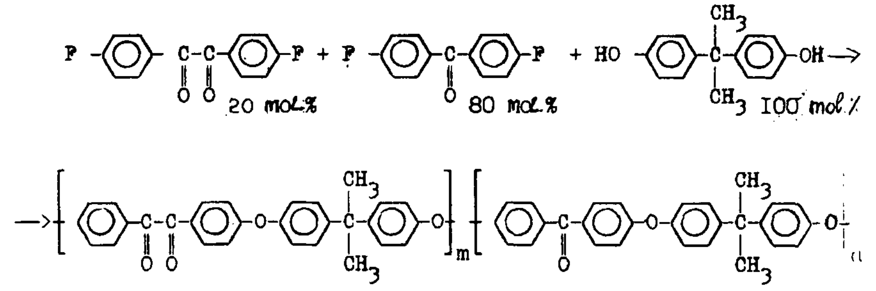


FIGURE 5 Influence of reaction time in DMAA at 180°C on of polyether-α-diketone based on 4,4′-DFB and bisphenol A.

It is also interesting to note that using the subsequent reagent introduction method (4.4'-DFB is added after azeotropic distillation from the water and toluene mixture and then cooling the reaction mixture to 20°C) and with an excess of K_2CO_3 both for a stoichiometric ratio of 4,4'-DFB and bisphenol A (Table I, N 10) and for a small excess of the first (Table I, N 9), partially crosslinked polymer is formed. We succeeded in obtaining highly soluble polymer with η_{inh} = 0.36 dL/g at the stoichiometric ratio of all reagents (Table I, N 11).

It is interesting to note, that gel formation takes place even when making copolymers based on 4,4'-DFB and 4,4'-difluorobenzophenone containing a small portion of α-diketone groups (20 mol %). Taking into account the data described above for the synthesis of polyether-α-diketones synthesis of copolyether-α-diketones was carried out in the DMAA medium for 5 hours at 170°C by sequentially adding 4,4'-DFB and 4,4'-difluorobenzophenone at concentration of app. 25 wt %.



Under such conditions polymer was obtained with η_{inh} = 0.67 dL/g (NMP) and soluble in common organic solvents (DMAA, m-cresol, symm-tetrachloroethane and so on). After dissolving this copolymer in chloroform, gel particles are visually observed which are not separated by the usual filtration: according to GPC data the gel content in the filtered off polymer reaches = 21.5% (Figure 6a).

In a similar reaction under the same conditions and by the use of 2,2'-DFB instead of 4,4'-DFB highly soluble high molecular (η_{inh} = 0.7 dL/g, NMP) linear polymers are obtained.

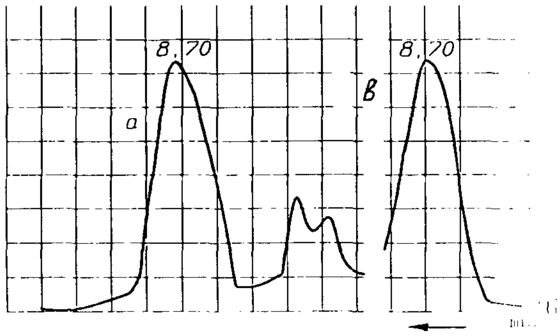
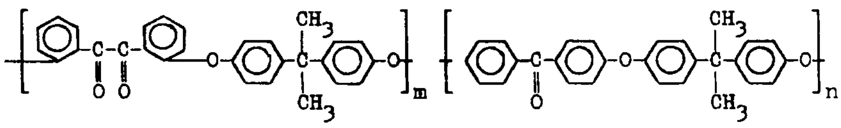


FIGURE 6 GPC-chromatograms of copolyetherketones with α-diketones moieties based on bisphenol A (100 mol %) and: a) 4,4'-difluorobenzyl (20 mol %) and 4,4'-difluorobenzophenone (80 mol %); and b) 2,2'-difluorbenzyl (20 mol %) and 4,4'-difluorobenzophenone (80 mol %) obtained in DMAA at 170°C.

These results indicate that the benzyl rearrangement in such a case is difficult or doesn't take place at all due to sterical factors:



From the GPC data microgel particles really are absent in given copolymer (Figure 6b) and polymer $\bar{M}_w$ reaches = 40000.

Synthesized homo- and copolymers are solid amorphous substances of white (copolymers) or yellow (linear polymers) or brown (network polymers) colour.

TABLE II

The mechanical properties of isotropic films of homo- and copolyether-α-diketones[a]

Polymer[b] No.	Tensile Strength, kG/cm^2	Elongation, %
6	540	5
6a[c]	560	87
6b[c]	600	12
9	490	3
11	210	1.5

[a] Films were out from 5% solution of polymer in chloroform.
[b] NN of polymers correspond to those in Table I.
[c] NN of copolymers correspond to those in Figure 6.

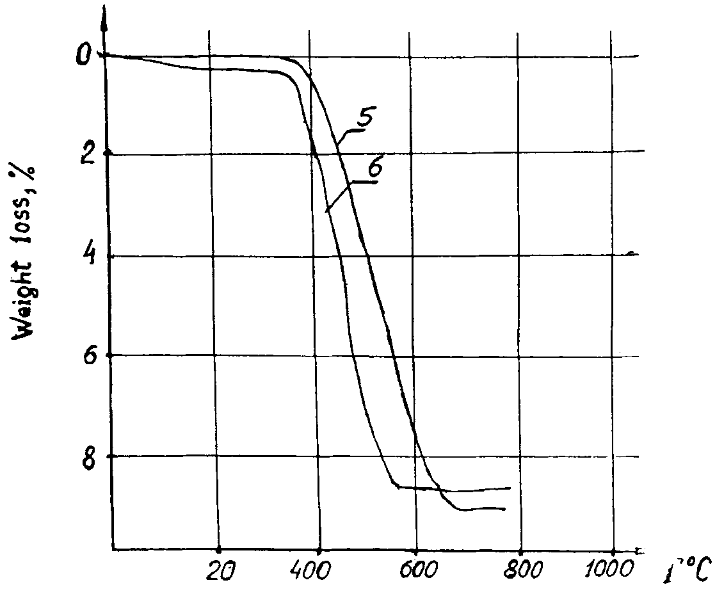


FIGURE 7 TGA of polyether-α-diketones (air; T = 5°C/min). The numbers of curves correspond to numbers of polymers in Table I.

From their solutions these homo- and copolymer-α-diketones form clear tough films (see Table II), having high dielectric properties ($\rho_v = 10^{14}$ Ohm cm).

Both linear and network polymers possess high thermal stability: temperature at which the weight loss reaches 5% (TGA data in air) is 370–400°C (Figure 7).

Thus amorphous high molecular thermostable poly-ether-α-diketones have been obtained. At the same time the availability of K_2CO_3 in the reaction medium in the presence of water gives rise to a benzyl rearrangement what can sufficiently make rather difficult the synthesis of such polymers, giving rise to branching and curing.

It results in a changing of the physical-chemical properties of polymers: they become insoluble in organic solvents, nonmeltable, etc.

To avoid or minimize side processes deriving from α-diketone linkages we can change process conditions and can introduce α-diketone groups by means of 2,2′-DFB instead of 4,4′-DFB.

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