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Polyketones containing indane structure elements

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Summary

Polyketones with indane structure elements were prepared by Friedel-Crafts polycondensation in three different reaction media. Only oligomers or insoluble material could be obtained, probably due to a side reaction of the indane ring, which leads to crosslinking at high conversion. The oligomers are soluble in common organic solvents such as THF and $CHCl_3$. Melting points, glass transition temperatures, and thermal stability of the oligomers were determined.

Introduction

Polymers containing aromatic keto groups are interesting materials because of their combination of good mechanical and thermal properties (1). In general, the degree of crystallinity of such polyketones is high, and therefore they are quite often insoluble at moderate temperatures. In some cases their melting temperature is close to their decomposition temperature so that processing from the melt is difficult. Both degree of crystallinity and melting temperature can be decreased by incorporation of flexible groups into the main chain like the ether or sulfone linkage, or by introducing kinks or bends (e.g. from *m*-substituted aromats) into the polymer backbone.

Polymers consisting of indane structure elements as repeating unit (polyindanes) proved to be amorphous and very stable at high temperatures in air (2,3), so we tried to synthesize polyketones containing the indane system in their backbones. These structures should improve the solubility of the polymers without affecting their thermal stability.

One possible access to polyketones is to use Friedel-Crafts acylation as a polycondensation reaction. In this case, monomers are activated aromats and acid chlorids. In processes like this, the solubilization of the polymers is achieved either by complexation of the carbonyl group by the catalyst (e.g. $AlCl_3$), or by protonation of this group by strong Brønsted acids (e.g. CF_3SO_3H, HF/BF_3).

Results and discussion

Polycondensation of 1,1,3-trimethyl-3-phenylindane with isophthalic and terephthalic acid chloride was achieved under different conditions using $AlCl_3$ as catalyst. Polymer **1a** was synthesized in boiling dichloromethane, for **2a** a melt of $AlCl_3$ and NaCl was used as solvent at 120°C, and **1b** and **2b** were produced in refluxing nitrobenzene. The reaction conditions are summarized in table 1, while table 2 gives some properties of the polymers.

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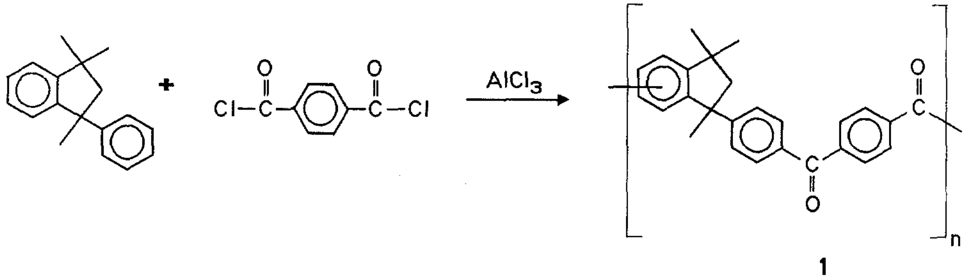

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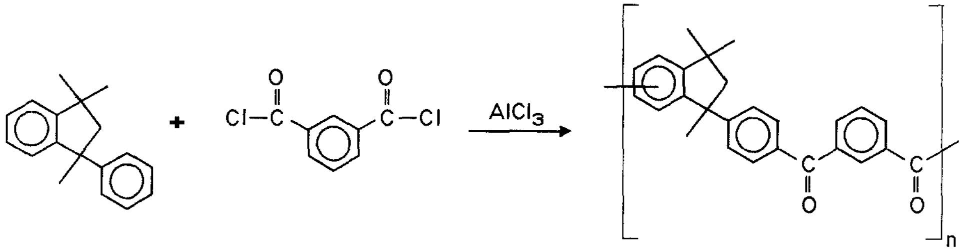

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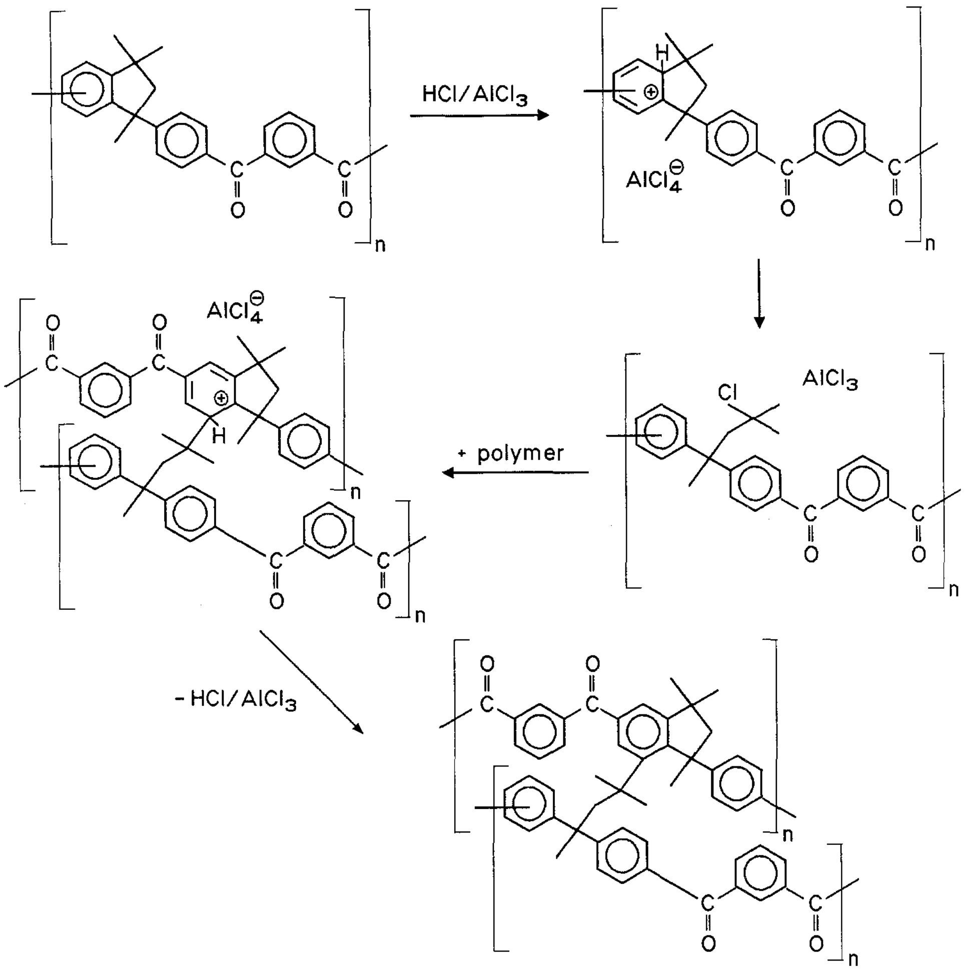
Table 1: Reaction conditions for the synthesis of polyketones with indane units

Product	Solvent	Temperature	Catalyst	Ratio $AlCl_3$/Carbonyl	Soluble fraction
1a	CH_2Cl_2	40°C	$AlCl_3$/LiCl	1.8	100%
1b	Nitrobenzene	70°C	$AlCl_3$	1.68	100%
2a	$AlCl_3$/NaCl melt	120°C	$AlCl_3$/NaCl	8.1	10%
2b	Nitrobenzene	70°C	$AlCl_3$	2.25	100%

Table 2: Properties of the polyketones **1** and **2**

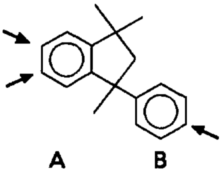
Product	$\overline{P}_n$(GPC)	$\overline{M}_n$	T_g	T_m	T_d (5% weight loss in air)
1a	18	2700	185°C	259°C	392°C
1b	9	1400			450°C
2a	6	900	165°C	–	343°C
2b	9	1400			407°C

The products **1a**, **1b**, and **2b** are completely soluble in THF, therefore GPC (polystyrene calibration) was used for determination of the molar masses. Polymer **2a** consists only of about 10% of THF-soluble products, the remaining product is insoluble in common organic solvents. Considering the high concentration of Lewis-acid within the $AlCl_3$/NaCl-melt and the reaction temperature of 120°C, it seems to be plausible that some structural defects are present in the insoluble parts of **2a**, which lead to branching and crosslinking. A possible pathway for such side reactions is shown below:



In the process outlined above, cyclic aliphatic structures are converted into linear aliphatic chains. Such chains generally decrease the thermal stability of the product. Indeed this effect can be observed here: **2a** starts to lose weight in air at 265°C, while **2b** is stable under the same conditions up to 370°C. In addition, the opening of the indane structure must cause a characteristic change in the ^{1}H NMR. This change can be observed even in the spectrum of the soluble part of **2a**. If the indane unit is intact, its methyl groups give rise to a characteristic pattern consisting of three singlets of equal intensity at 1.1, 1.4, and 1.8 ppm. In the proton NMR of **2a**, however, it can be seen clearly that there are additional signals beneath the singlet at 1.4 ppm. These signals are caused by two of the three methyl groups of the linear aliphatic structure element, which are expected to absorb in the region around 1.35 ppm (4).

Another possible origin of crosslinking can be multiple acylation of phenylindane. Each ring is deactivated for further acylation once it is acylated, and phenylindane is difunctional as it contains two independent phenyl rings. Under more drastic reaction conditions, however, multiple acylation of the rings may occur.



bold arrow: activated, no steric hindrance
dotted arrow: activated, steric hindrance

Especially ring **A** may not be sufficiently deactivated, because of the presence of two alkyl substituents. This is the main reason for the difficulties in finding adequate reaction conditions for controlled polyketone formation: if the conditions are too mild, conversion may stay below 90%, resulting only in oligomers. Conditions which allow to push the conversion close to 99% may result in multiple acylation and therefore crosslinking.

A combination of both sidereactions, multiple acylation and ring cleavage with subsequent Friedel-Crafts alkylation, is most likely responsible for the formation of mostly crosslinked product under the conditions described for **2a**.

The structure of product **2b** is closer to the expected composition. Both ^{1}H NMR and ^{13} NMR show the signals which are typical for the 1,1,3-trimethyl-3-phenylindane system. The intensities of the peaks in the proton NMR are in agreement with the expected ratios. Splitting of the methyl- and methylene peaks in proton and carbon NMR indicates the presence of several isomers. This is not unexpected, as there are more than two positions in the 1,1,3-trimethyl-3-phenylindane unit which are activated towards Friedel-Crafts acylation, as is indicated by the arrows in the scheme above.

The molar masses of **2b** and the soluble fraction of **2a** are rather low. GPC (polystyrene standards) shows that the degree of polymerization of **2b** is $\overline{P}_n \approx 8$ and for the soluble fraction of **2a** $\overline{P}_n \approx 5$. DSC measurements show **2b** to be amorphous with $T_g = 165^oC$ at a heating rate of 20 K/min. No melting endotherm can be detected.

Polymer **1b**, which was synthesized in nitrobenzene with $AlCl_3$ as Friedel-Crafts catalyst under the same conditions as **2b**, also possesses a degree of polymerization of $\overline{P}_n \approx 8$. Its ^{1}H NMR shows the signals of the indane system with some splitting due to isomers. In addition, at 3.92 ppm the signal of the methylester end group is detected. This end group is formed by the reaction of residual acid chloride functions with methanol during precipitation. A comparison of the intensities of the signals of the end group and a methyl group of the backbone yields a degree of polymerization of $\overline{P}_n \approx 8.5$, which is in good agreement with the value obtained from GPC. The signals of the carboxyl- and the methyl carbon atoms of the ester end group can be seen at 165.8 and 52.0 ppm.

Both proton and carbon NMR of **1b** are free from any additional signals in the aliphatic region besides those which are caused by the indane system. This proves that the indane ring is not affected by the polymerization. Polymer **1b** suffers a 5% weight loss in air at 450°C (heating rate 10K/min). It is partly crystalline with $T_g = 185^oC$ (20 K/min) and $T_m = 259^oC$.

In contrast to **1b**, **1a** seems to possess some structural defects, as is shown by its proton and carbon NMR's. They contain several small additional signals of low intensity in the aliphatic region, which can not be assigned to the indane system. Thermogravimetry shows that the thermal stability of **1a** is considerably poorer than that of **1b**: **1a** exhibits a 5% weight loss at 392°C in air.

As **1a** is synthesized in methylene chloride, there is the possibility of incorporation of methylene groups as linkages between aromatic rings by Friedel-Crafts alkylation. Such groups should give rise to signals at 3.85 ppm in the proton NMR and 41.9 ppm in the carbon NMR. However, no such signals are detected. The participation of methylene chloride in the polymerization reaction can therefore be excluded in this case (within the limits of quantitative NMR spectroscopy). This is in agreement with the observation of other authors (5), that the presence of a Lewis base in addition to $AlCl_3$ can prevent alkylation of the reactants by the solvent.The degree of polymerization of **1a** is $\overline{P}_n$ = 18; which is the highest value obtained in this investigation. This fact and the partial cleavage of the indane ring is probably due to the higher catalyst concentration compared to the synthesis of **1b** and **2b**.

Conclusion

The results reported above show the difficulties in obtaining polyketones with indane structure elements by Friedel-Crafts acylation. Altogether, nitrobenzene as a solvent and $AlCl_3$ as the catalyst gave the most regularly structured products, but in order to obtain higher $\overline{P}_n$'s it seems necessary to use more drastic reaction conditions. Unfortunately this increases the probability of partial cleavage of the aliphatic ring and crosslinking through multiple acylation. However, these problems might be avoided by using different catalysts such as CF_3SO_3H or HF/BF_3. If strong proton acids are used as catalysts, the solubilization of the polymer is achieved by protonation of the carbonyl groups. One can expect that protonated keto groups are considerably more deactivating than normal keto groups or those which are complexed by Lewis acids. Therefore multiple acylation or ring cleavage by protonation of phenyl ring should be less likely.

Experimental

All preparations were carried out under nitrogen atmosphere. Dichloromethane was dried by distilling from calcium hydride. Nitrobenzene was dried by distilling from P_2O_5. The synthesis of 1,1,3-trimethyl-3-phenylindane is achieved in a similar way as is described in ref. (6) for 1-methyl-3-phenylindane.

Polymerizations

Poly(1,4-phenylene-carbonyl-1,4-phenylene-3,5(6)-indanylene-carbonyl) 1a

In a round bottom flask with nitrogen inlet and reflux condenser 2.9 g (12.29 mmol) of 1,1,3-trimethyl-3-phenylindane and 2.5 g (12.31 mmol) of terephthalic acid chloride are dissolved in 150 ml of dichloromethane. To this solution 6.0 g (45 mmol) of $AlCl_3$ and 2.0 g (47 mmol) of LiCl are slowly added under stirring. Then the mixture is heated to reflux and stirred at this temperature for 12 h. After cooling to room temperature, the mixture is poured into 500 ml of 18% hydrochloric acid. The organic layer is separated, washed with water and poured into 500 ml of ethanol to precipitate the polymer. After filtration the product is dried in vacuo at 100°C.

Yield: 2.95 g (66%)

GPC: $\overline{M}_n$ = 2700; $\overline{M}_w/\overline{M}_n$ = 1.9

Thermogravimetry: (Heating rate 10 K/min) T_d = 382°C (first loss of weight)
$T_{d5\%}$ = 392°C (5% weight loss)

IR: 2959, 2926, 2864, 1728, 1661, 1603, 1402, 1312, 1275, 1242, 930 cm^{-1}

^{1}H-NMR: δ (ppm) = 1.1 (s; $C\underline{H}_3$); 1.4 (s; $C\underline{H}_3$); 1.8 (s; $C\underline{H}_3$); 2.325 (d, J = 12.5 Hz; $C\underline{H}_2$); 2.465 (d, J = 12.5 Hz; $C\underline{H}_2$); 3.95 (s; $O{-}C\underline{H}_3$, end group); 7.1-8.1 (m; aromat); additional signals without assignment: 1.2-1.7; 1.95; 3.32; 4.4

^{13}C-NMR: δ (ppm) = 29.9-30.6 ($\underline{C}H_3$); 43.0-43.2 ($\underline{C}(CH_3)_2$); 51.0-51.3 ($\underline{C}(CH_3)(Ph)$); 52.0 ($O{-}\underline{C}H_3$, end group); 122.8; 124.7; 124.8; 126.6; 128.4; 129.5; 130.0; 130.2; 130.4; 132.9; 134.5; 136.0; 136.6; 140.6; 140.9; 148.6; 152.8;

153.6; 155.6; 157.7; 195.4-195.8 ($\underline{C}$=O); additional signals in the aliphatic region without assignment: 13.5; 14.5; 24.3; 36.5; 49.5; 61.2

Elemental analysis:

	%C	%H	%O
found :	83.96	6.18	9.50
calc. for $\overline{P}_n = 18$:	83.91	6.00	10.08

(two methyl ester end groups)

Poly(1,3-phenylene-carbonyl-1,4-phenylene-3,5(6)-indanylene-carbonyl) 2a

In a round bottom flask with nitrogen inlet and gas outlet 4.1 g (17.2 mmol) of 1,1,3-trimethyl-3-phenylindane, 3.5 g (17.2 mmol) of isophthalic acid chloride, 15.5 g (116mmol) of $AlCl_3$ and 10.8 g (185 mmol) of NaCl are heated to 120°C, where the mixture becomes liquid. This temperature is maintained for 2 h. HCl evolution was observed during this time. Then the mixture is poured into 850 ml of 18%hydrochloric acid to remove the catalyst. The precipitated polymer is dissolved in 400 ml of $ChCl_3$. Thje organic layer is separated, washed with water, and poured into 800 ml of ethanol to precipitate the polymer.

Yield: 4.95 g (78%)

GPC: $\overline{M}_n = 900$; $\overline{M}_w/\overline{M}_n = 1.9$

Thermogravimetry: (Heating rate 10 K/min) T_d = 264°C (Beginning of weight loss)
$T_{d5\%}$ = 343°C (5% weight loss)

IR: 2959, 2926, 2864, 1730, 1661, 1601, 1576; 1456; 1317, 1236; 712 cm^{-1}

^{1}H-NMR: δ (ppm) = 1.08 (s; $C\underline{H}_3$); 1.39 (s; $C\underline{H}_3$); 1.75 (m; $C\underline{H}_3$); 2.285 (d, J = 12.5 Hz; $C\underline{H}_2$); 2.505 (d; J = 12.5 Hz; $C\underline{H}_2$); 7.0-8.3 (m; aromat); additional signals without assignment: 1.2-1.54; 1.95; 2.65; 3.0-3.5; 3.8-4.2

^{13}C-NMR: δ (ppm) = 30.1-30.6 ($\underline{C}H_3$); 42.9-43.1 ($\underline{C}(CH_3)_2$); 50.8-51.2 ($\underline{C}(CH_3)(Ph)$); 52.2 (O—$\underline{C}H_3$, end group); 58.7 ($\underline{C}H_2$); 122.7; 124.1; 124.5-124.7; 126.6; 128.3; 129.2-130.1; 131.0; 132.7; 133.2; 134.5; 136.0; 136.6; 136.8; 137.6-138.1; 148.4; 152.8; 153.5; 155.4; 157.6; 195.1-195.5 ($\underline{C}$=O); additional signals without assignment: 15.9; 24.3; 45.0; 45.7; 52.2; 53.1

Elemental analysis:

	%C	%H	%O
found :	85.29	6.10	9.29
calc. for $\overline{P}_n = 6$:	86.32	6.49	7.19

(two indane end groups)

Poly(1,4-phenylene-carbonyl-1,4-phenylene-3,5(6)-indanylene-carbonyl) 1b

In a round bottom flask with nitrogen inlet 4.72 g (20 mmol) of 1,1,3-trimethyl-3-phenylindane and 4.0 g (20 mmol) terephthalic acid chloride are dissolved in 100 ml of nitrobenzene. After addition of 9.0 g (67 mmol) of $AlCl_3$ the solution is heated for 1 h to 40°C and for 10h to 70°C. After cooling to room temperature, the mixture is poured into 500 ml of 18% hydrochloric acid. The organic layer is removed and poured into 500 ml of methanol to precipitate the polymer.

Yield: 5.88 g (81%)

GPC: $\overline{M}_n = 1400$; $\overline{M}_w/\overline{M}_n = 1.4$

DSC: (Heating rate 20 K/min) T_g = 185°C; T_m = 259°C

Thermogravimetry: (Heating rate 10 K/min) T_d = 420°C (Beginning of weight loss)
$T_{d5\%}$ = 450°C (5% weight loss)

IR: 2959, 2926, 2864, 1728, 1661, 1603, 1402, 1312, 1275, 1242, 930 cm^{-1}

^{1}H-NMR: δ (ppm) = 1.1 (s; $C\underline{H}_3$); 1.37 (s; $C\underline{H}_3$); 1.7-1.76 (m; $C\underline{H}_3$); 2.2-2.53 (m; $C\underline{H}_2$); 3.92 (s; O—$C\underline{H}_3$); 7.1-8.1 (m; aromat)

^{13}C-NMR: δ (ppm) = 30.2-30.8 ($\underline{C}H_3$); 43.0-43.3 ($\underline{C}(CH_3)_2$); 50.8-51.2 ($\underline{C}(CH_3)(Ph)$); 52.2

(O–$\underline{C}H_3$), end group); 58.9 ($\underline{C}H_2$); 122.8; 124.8; 125.7; 126.4; 126.7; 127.0; 128.1; 129.6; 130.0; 130.2; 130.4; 133.0; 143.5; 136.0; 136.8; 140.6; 140.9; 148.6; 152.7; 153.2; 155.6; 157.9; 195.5-195.9 ($\underline{C}$=O);

Elemental analysis:

	%C	%H	%O
found :	83.53	6.47	9.95
calc. for $\overline{P}_n$ = 6 :	83.87	6.24	9.90

(one methyl ester end group)

Poly(1,3-phenylene-carbonyl-1,4-phenylene-3,5(6)-indanylene-carbonyl) 2b

In a round bottom flask with nitrogen inlet 4.72 g (20 mmol) of 1,1,3-trimethyl-3-phenylindane and 4.0 g (20 mmol) isophthalic acid chloride are dissolved in 100 ml of nitrobenzene. After addition of 12.0 g (90 mmol) of $AlCl_3$ the solution is heated for 1 h to 40°C and for 10h to 70°C. After cooling to room temperature, the mixture is poured into 500 ml of 18% hydrochloric acid. The organic layer is removed and poured into 500 ml of methanol to precipitate the polymer.

Yield: 6.2 g (85%)

GPC: $\overline{M}_n$ = 1400; $\overline{M}_w/\overline{M}_n$ = 1.3;

DSC: (Heating rate 20 K/min) T_g = 165°C;

Thermogravimetry: (Heating rate 10 K/min) T_d = 370°C (Beginning of weight loss)
$T_{d5\%}$ = 407°C (5% weight loss)

IR: 2958; 2926; 2864; 1730; 1661; 1603; 1572; 1456; 1406; 1315; 1232; 711 cm^{-1}

^{1}H-NMR: δ (ppm) = 1.09 (s; $C\underline{H}_3$); 1.39-1.41 (m; $C\underline{H}_3$); 1.69-1.77 (m; $C\underline{H}_3$); 2.2-2.52 (m; $C\underline{H}_2$); 7.0-8.5 (m; aromat)

^{13}C-NMR: δ (ppm) = 30.0-30.1 ($\underline{C}H_3$); 42.5-43.1 ($\underline{C}(CH_3)_2$); 50.2-51.1 ($\underline{C}(CH_3)(Ph)$); 58.9 ($\underline{C}H_2$); 122.5; 122.6; 124.2-124.8; 125.5; 126.1-126.8; 128.0; 128.1; 129.2; 129.8-130.0; 131.0; 133.2; 134.5; 135.5-135.7; 136.6; 137.8-138.0; 147.7; 148.3; 149.2; 149.9; 152.0; 152.8; 153.5; 154.8; 155.5; 156.5; 157.8; 195.0-195.9 ($\underline{C}$=O)

Elemental analysis:

	%C	%H	%O
found :	83.93	6.20	8.06
calc. for $\overline{P}_n$ = 8 :	86.08	6.40	7.52

(two indane end groups)

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