

Polycondensation of benzyl chloride catalysed by $\text{ArCr}(\text{CO})_3$

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Arene chromium tricarbonyls were found to function as effective homogeneous catalysts for the polycondensation of benzyl chloride when they are thermally activated. The catalytic activity and induction period depended upon the nature of the arene attached to the metal. Their activity decreased and induction time increased with respect to the nature of the arene in the order: anisole, toluene, *p*-xylene and benzene. The alkylation products of a model reaction, catalysed by $\text{ArCr}(\text{CO})_3$, were only *ortho*- and *para*-substituted. The degree of polybenzyl branching, determined by ^1H n.m.r. and *DP*, was found to increase with increasing reaction temperature and M_n . Although there is experimental evidence that in the initiation step the arene ring remains loosely attached to the metal, a mechanism similar to that of polymerization by a Lewis acid catalyst is proposed.

Keywords Polycondensation; polymer characterization; mechanism, catalytic activity

INTRODUCTION

Interest in the synthesis of polybenzyls has probably been maintained by the availability of the relatively inexpensive benzyl chloride and by the fact that linear high molecular weight polybenzyls may lead to high-temperature application materials, useful in the aerospace industry.

The polymerization of benzyl chloride has been studied mainly with systems that involve conventional Lewis acid catalysts¹⁻⁸ such as AlCl_3 , SnCl_4 , TiCl_4 and SbF_5 , in the presence of group IIA metal oxides⁹, and under the influence of organoaluminium compounds¹⁰⁻¹².

It has been previously shown^{13,14} that arene tricarbonyl molybdenum, a group VIB complex, possesses Lewis acid properties and is an effective homogeneous catalyst for Friedel-Crafts reactions. It offers some advantages over ordinary Lewis acid catalysts, particularly in ease of handling and storage, reaction work-up, and in its being somewhat milder than aluminium chloride.

The bulk of this work was devoted to the investigation of the polymerization of benzyl chloride catalysed homogeneously by a variety of arene chromium tricarbonyls. We chose these complexes because we found that they are milder and exhibit a remarkable thermal stability (170°C) relative to molybdenum and tungsten analogues.

EXPERIMENTAL

Materials

The benzyl chloride monomer was purchased from Fluka Chemical Co. and vacuum distilled before use. Toluene (Fluka) was distilled over lithium aluminium hydride. The arene chromium tricarbonyls (arene: aniline, anisole, benzene, toluene and *p*-xylene) were obtained from Pressure Chemical Co. and used as received. All solvents were reagent grade and used without further purification.

Physical methods

Infra-red spectra were recorded on a Perkin-Elmer model 180 i.r. spectrophotometer; the compounds were sampled as thin films on KBr plates. The ^1H n.m.r. spectra were recorded on a pulsed Fourier transform n.m.r. spectrometer, a Varian XL-200, operating at a frequency of 200 MHz. Samples were prepared as 5% w/v solutions in CDCl_3 containing 0.01% TMS as an internal standard. The spectra were recorded under the following conditions: pulse width, 6 μs (90°); data points, 15 680; spectrum width, 2800 Hz; acquisition time, 2.80 s; pulse repetition time, 30 s; number of transients, 10. The molecular weights (osmometric) and elemental analyses were obtained commercially.

Polymerization of benzyl chloride

All reactions were conducted in the same manner. A typical run was as follows. A 25 ml, three-necked, round-bottomed flask was equipped with a thermometer, a nitrogen gas inlet and a Graham type condenser. The condenser was fitted with a gas adaptor. A tygon tubing, connected to the gas adaptor, was immersed into a flask containing 1000 ml distilled water. Degassed benzyl chloride, 20 ml (160 mmol), and 1 mmol of arene chromium tricarbonyl was placed in the flask. The apparatus was purged with dry nitrogen for 10-15 min while the contents of the flask were constantly stirred by means of a magnetic stirrer. The mixture was then heated to the required temperature by means of an oil bath, and the temperature was maintained with the aid of a temperature regulator to an accuracy of $\pm 1^\circ\text{C}$ until the HCl gas evolution ceased. The polymeric material obtained was removed from the flask by extraction with methylene chloride. The solution was then concentrated on the rotary evaporator and purified by chromatography on a 2×50 cm silica gel column with methylene chloride as the eluting solvent. The eluent was concentrated down to 50 ml and the polymer present in the eluent was precipitated twice, first in 500 ml methanol

Table 1 Polymerization of benzyl chloride by arene $\text{Cr}(\text{CO})_3$ catalysts^a

Sample	Arene	Temp. (°C)	Time	Conversion (%)	Yield (%)	Soft. pt (°C)	Colour	Analysis ^b		
								\bar{M}_n	%C	%H
PB1	Anisole	100	66 h	22.3	15.2	67–70	Grey–yellow	6100	90.88	6.88
PB2	Anisole	120	24 h	73.2	48.6	70–74	Beige	7080	91.25	6.97
PB3	Anisole	140	130 min	91.6	66.7	61–64	Lemon yellow	9500	92.74	7.04
PB4	Anisole	160	30 min	93.7	54.2	62–65	Yellow	7300	92.91	7.00
PB5	Toluene	100	68 h	16.2	12.1	62–64	Grey–yellow	6800	90.97	6.83
PB6	Toluene	120	28 h	70.7	60.4	67–70	Beige	7000	92.90	6.85
PB7	Toluene	140	265 min	77.0	64.6	66–70	Lemon yellow	7740	92.35	6.94
PB8	Toluene	160	40 min	92.3	32.6	64–67	Yellow	5310	92.99	6.98
PB9	<i>p</i> -Xylene	100	69 h	12.1	6.9	87–90	Yellow	5200	92.66	6.88
PB10	<i>p</i> -Xylene	120	43 h	67.4	61.1	61–65	Grey–yellow	7850	91.06	6.82
PB11	<i>p</i> -Xylene	140	280 min	81.1	63.2	72–76	Orange	8460	92.89	7.04
PB12	<i>p</i> -Xylene	160	45 min	92.5	59.0	55–59	Beige	4320	91.48	6.80
PB13	Benzene	100	72 h	7.8	4.5	65–67	Yellow	3420	92.61	6.94
PB14	Benzene	120	45 h	66.4	54.9	69–73	Green–yellow	8100	91.40	6.90
PB15	Benzene	140	295 min	88.6	70.8	67–70	Orange–yellow	8280	92.57	7.01
PB16	Benzene	160	45 min	91.4	50.0	57–60	Lemon yellow	3690	93.01	6.98

^a Conditions: 160 mmol PhCH_2Cl and 1.0 mmol catalyst

^b Theoretical values: C, 93.34%; H, 6.66%

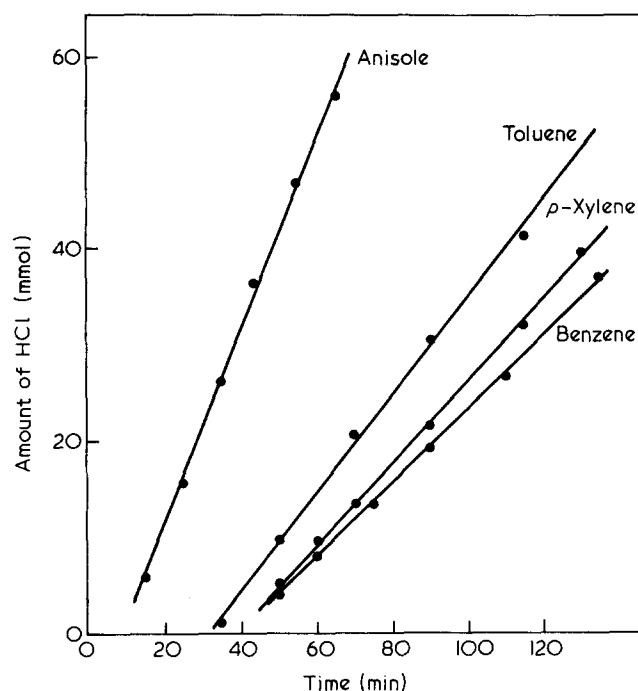


Figure 1 Amount (mmol) HCl gas evolved for the polymerization of PhCH_2Cl by various arene $\text{Cr}(\text{CO})_3$ catalysts at 140°C

and then in hexane. The resulting polymer was vacuum dried to constant weight at room temperature. Then 1 litre distilled water, containing the evolved HCl gas, was titrated with standard NaOH solution to the phenolphthalein end point.

The effect of temperature on the activity of different catalysts was investigated in order to optimize the polymerization conditions. The results of these studies are presented in Table 1.

Method of following HCl evolution

The purpose of this experiment was to study the amount of hydrogen chloride evolved from the

Table 2 Percentage yield and isomer distribution of tolylphenylmethane prepared from toluene and benzyl chloride with $\text{ArCr}(\text{CO})_3$ catalysts^a

Arene	Yield (%)	Isomer (%)		
		<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
<i>p</i> -Xylene	15.6	41	0	59
Toluene	10.4	45	0	55
Benzene	18.3	47	0	53
Anisole	6.2	48	0	52
Aniline	0	0	0	0

^a Conditions: 140 mmol toluene, 80 mmol benzyl chloride, 1.0 mmol catalyst, reflux temp. 122°C

polymerization of benzyl chloride catalysed by different $\text{ArCr}(\text{CO})_3$ catalysts as a function of time at constant temperature (140°C), 1 mmol of catalyst and 160 mmol of monomer. The polymerization was carried out as described above. At time intervals, samples of the hydrochloric acid aqueous solution were withdrawn and titrated with 0.01 N sodium hydroxide solution to the phenolphthalein end point. The amount of HCl gas evolved (mmol) vs. time for a series of arene chromium tricarbonyl catalysts is depicted in Figure 1.

Alkylation of toluene with benzyl chloride

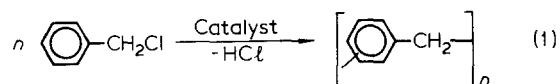
The purpose of this study was to determine the effect of different $\text{ArCr}(\text{CO})_3$ catalysts on the isomer distribution for the alkylation of toluene with benzyl chloride. The reaction was carried out in a solution consisting of 15 ml (140 mmol) of toluene, 10 ml (80 mmol) of benzyl chloride and 1.0 mmol of catalyst. The reaction mixture was refluxed (122°C) until HCl evolution ceased. The reaction system was then dismantled, cooled to room temperature, filtered and the filtrate was fractionally distilled (0.1 torr). The fraction in the 85°–88°C range was collected and identified by i.r. and n.m.r. as tolylphenylmethane. The relative isomer distribution was determined by ¹H n.m.r. and the data are recorded in Table 2.

RESULTS AND DISCUSSION

General considerations

The first approach taken was to investigate the optimum polymerization conditions such as temperature and different catalysts. The experimental data are summarized in *Table 1*.

For reaction (1), for each mole of benzyl chloride reacted one mole of hydrochloric acid is consumed.



Therefore, the percentage conversion, based on the amount of HCl evolved, can be determined by the ratio of millimoles HCl evolved and millimoles benzyl chloride used, assuming the end-groups contain negligible amounts of chlorine. The amount of HCl released was determined by collecting the evolved HCl gas into distilled water and titrating with NaOH solution using phenolphthalein indicator. The amount of polymer produced for every reaction is based on the polymer recovered after having passed the reaction product through a silica column, precipitation in methanol, followed by a second precipitation in hexane and dried under vacuum to a constant weight.

As can be seen in *Table 1*, arene chromium tricarbonyls function as effective homogeneous catalysts for the polymerization of benzyl chloride when they are thermally activated. The minimum temperature required for these organometallics to possess some catalytic activity is about 100°C. Furthermore these species are truly catalytic, since small amounts are needed for the polymerization; this probably indicates that the active form of the catalyst retains its structure and activity after each reaction sequence. This is important as it eliminates side reactions, and the problem of catalyst removal is alleviated considerably.

The percentage conversion increases substantially as the reaction temperature increases but it levels off at about 94%. This may be due to the fact that the growing chloromethyl units become increasingly buried as conversion progresses. The yield and \bar{M}_n of purified polybenzyls increases with conversion but when the reaction temperature increased to 160°C the conversion increased whereas the yield and \bar{M}_n dropped. This probably is attributed to side reactions which become predominant and compete effectively with the growth of the polymer chains. The nature of the arene attached to the $\text{Cr}(\text{CO})_3$ appears to have some control over conversion, especially at lower temperatures. It is of interest to note that aniline chromium tricarbonyl did not show any catalytic activity when it was allowed to react with benzyl chloride at 120°C for 55 h. Instead, a small amount of precipitate was formed which was probably the result of nitrogen complexation with benzyl chloride producing an insoluble salt. A series of reactions, consisting of toluene, benzyl chloride and $\text{ArCr}(\text{CO})_3$ catalyst, were run in order to determine the selectivity of each catalyst towards the formation of *ortho*-, *meta*- and *para*-isomers. The results, presented in *Table 2*, show that no *meta*- was formed and the *para*- was higher than the *ortho*-isomer. However, there are no significant changes in these distributions from one catalyst to the next. Again, aniline chromium tricarbonyl was inactive. The

percentage yield of tolylphenylmethane (*Table 2*) decreased as the catalytic activity increased. Perhaps this is due to the catalytic activity which allows side reactions such as polybenzyl formation to predominate.

Although all polymerizations recorded in *Table 1* were run neat, attempts to polymerize benzyl chloride in inert solvents of low dielectric constant such as heptane were made, but unfortunately as soon as the polymer was formed it precipitated out in a highly crosslinked form.

All polybenzyls (*Table 1*) softened in the 55°–90°C range and became liquids above 120°C. Their physical appearance, texture and colour differ markedly. However, when they are excited in solution with short-wave ultra-violet light, they all fluoresce blue light. Their elemental analyses agree fairly well with the theoretical values (C, 93.34%; H, 6.66%). The solubility of these polybenzyls varied. They were insoluble in aliphatic hydrocarbons and alcohols such as hexane, heptane, methanol and ethanol. In other solvents, such as methylene chloride, chloroform, benzene and chlorobenzene, solubility was good to moderate.

The catalytic activity of the chromium complex for the polymerization of benzyl chloride was found to depend on the nature of the arene attached to the metal. A study was carried out to determine the rate of HCl evolution for the polymerization of 20 ml benzyl chloride by different $\text{ArCr}(\text{CO})_3$ catalysts as a function of time at 140°C and 1 mmol of catalyst. The results are depicted in *Figure 1*. All runs were carried out to approximately 30% conversion to avoid considerable catalyst decomposition and high-viscosity interference. The fastest rate was found for anisole, followed by toluene, *p*-xylene and benzene. The rate of HCl evolution (*Table 3*) with anisole as the coordinated arene on the metal was almost three times faster than the rate based on the coordinated benzene. The induction periods were determined by two methods: (a) from the intercept on the time axis of the plots of HCl evolution as a function of time and (b) from the time the reaction solution turned from yellow to orange, followed by gas evolution. As shown in *Table 3*, the agreement between the two methods was quite good, accounting for the solubility of hydrochloric acid in the reaction mixture. The induction period increased as the temperature decreased. At temperatures lower than 140°C the HCl evolution was too slow, whereas over 140°C it was too fast and could not be followed easily. All these observations are similar to those found for the selective hydrogenation of conjugated dienes to *cis*-monoenes catalysed by arene chromium tricarbonyls, where it was reported¹⁵ that the induction time and rate of hydrogenation were controlled by the nature of the arene attached on chromium.

Table 3 Catalytic activity of $\text{ArCr}(\text{CO})_3$ in the polymerization of PhCH_2Cl at 140°C

Arene	Approximate induction time (min) based on		Rate HCl (mmol min ⁻¹)
	Solution colour change	Intercept	
Anisole	6	8	2.54
Toluene	27	31	1.28
<i>p</i> -Xylene	31	37	1.08
Benzene	32	39	0.94

Table 4 Polybenzyl branching

Sample	Relative branching ^a			Terminal ^b protons (%)	Quantitative branching		Terminal ^c protons (%)
	A:B	C:B	C:A		X	\overline{DP}	
PB1	0.37	1.79	4.84	17.1	8.4	68	17.2
PB2	0.43	1.70	3.95	20.2	11.4	79	20.2
PB3	0.62	1.52	2.45	29.6	23.6	106	28.9
PB4	0.65	1.48	2.27	30.5	18.9	81	30.6
PB5	0.32	1.80	5.62	18.4	8.2	76	15.1
PB6	0.42	1.73	4.11	23.9	11.2	78	19.5
PB7	0.57	1.56	2.73	25.4	17.5	86	26.8
PB8	0.58	1.50	2.58	30.9	12.2	59	27.8
PB9	0.38	1.94	5.10	15.3	6.6	58	16.3
PB10	0.45	1.72	3.82	19.5	13.4	87	20.6
PB11	0.60	1.60	2.67	27.1	19.5	94	27.2
PB12	0.64	1.51	2.36	28.1	10.6	48	30.1
PB13	0.50	1.70	3.40	19.4	5.9	38	22.5
PB14	0.51	1.69	3.30	21.3	15.8	90	23.5
PB15	0.56	1.65	2.95	29.3	17.7	92	25.4
PB16	0.67	1.50	2.24	29.8	9.2	41	30.9

^a A = area of monosubstituted phenyls (δ : 7.16); B = area of methylene groups (δ : 3.97); C = area of multisubstituted phenyls (δ : 6.94–7.04)

^b Determined from equation (2); X = number of branches, \overline{DP} = degree of polymerization, determined from \overline{M}_n

^c Determined from equation (4)

Characterization of polybenzyls

A systematic i.r. structure analysis of polybenzyls has been conducted by Haas¹⁶ and recently in Lenz's laboratory⁸. Monosubstituted benzenes generally show two strong absorption bands in the 675–700 cm⁻¹ and 725–775 cm⁻¹ regions, whereas *para*-disubstituted derivatives show a strong peak in the 800–860 cm⁻¹ range. Investigation of the i.r. spectra of *o*-, *m*- and *p*-dibenzylbenzene model compounds reveal that the bands at 1050, 1090 and 1023 cm⁻¹ are specific for *o*-, *m*- and *p*-dibenzylbenzene isomers respectively and the peak at 1032 cm⁻¹ is characteristic of monosubstituted benzyl pendant groups⁸.

On a qualitative basis, the i.r. spectra of all polybenzyls prepared in this work appear to be identical regardless of the synthetic conditions employed. They exhibit vibrations in the 1019, 1028, 1070 and 1100 cm⁻¹ regions. Other i.r. bands of less structural importance appear in the 3000–3100 cm⁻¹ range arising from the aromatic CH stretching modes. The band with the strong intensity peak at 2910 cm⁻¹ is due to the CH stretching mode of the methylene group. The skeletal vibrations involving carbon-carbon stretching within the ring absorb at 1600–1580 cm⁻¹ and 1400–1520 cm⁻¹. The region between 1700 and 2000 cm⁻¹ represents substituted aromatic ring vibrations.

It has been reported¹⁷ that polybenzyls containing completely *para* structures may not exhibit the *para* substitution pattern in the i.r. spectrum and the absence of such bands may be due to the conformational factors of the polymer. For this reason structure characterization of polybenzyls based only on i.r. spectra may not be a reliable approach and the assigned bands should be treated with caution.

All polybenzyls prepared in this work were analysed by ¹H n.m.r. spectroscopy and examined for relative and quantitative branching. The relative degree of branching was determined by computing the ratio of ¹H n.m.r. peak area (A) of mono-substituted phenyl (δ : 7.16) to the area (B) of methylene group (δ : 3.96); from the ratio of the ¹H n.m.r.

peak area (C) of the multisubstituted phenyl groups (δ : 6.96–7.04) to the methylene group (δ : 3.96); and finally from the ¹H n.m.r. peak area ratio of the multisubstituted to monosubstituted phenyls. The results appear in Table 4. The smaller the A:B ratio the lower the degree of branching because the terminal groups of all short branches consist of monosubstituted benzene rings. On the other hand, the higher the C:B and C:A ratios the less the branching. The percentage of hydrogens on terminal benzyls can be estimated from:

$$\text{hydrogens on terminal benzyls (\%)} = \frac{A}{A+C} \times 100 \quad (2)$$

Quantitatively, the number of branches in each polymer sample was calculated by equation (3) below. This equation has been used by Kuo and Lenz¹⁸ to determine the degree of branching for a number of polybenzyls prepared from the polymerization of 2-chloroethylbenzene with AlCl₃ catalyst.

$$\frac{4[\overline{DP} - (X+1)] - X}{5(X+1)} =$$

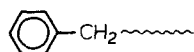
$$\frac{{}^1\text{H n.m.r. area of multisubstituted benzene rings}}{{}^1\text{H n.m.r. area of monosubstituted benzene rings}} \quad (3)$$

where X represents the number of branches and (X+1) the monosubstituted benzene rings. Hence, the total number of protons on the terminal benzyls is 5(X+1) whereas the number of protons on multisubstituted benzene rings will be 4[$\overline{DP} - (X+1)$] - X, since for every branch generated one hydrogen is lost from the chain. The degree of polymerization is denoted by \overline{DP} and was determined from the number average molecular weight (\overline{M}_n). Therefore

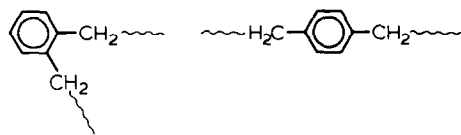
$$\begin{aligned} & \text{hydrogens on terminal benzy ls (\%)} \\ & = \frac{5(X+1)}{5(X+1) + 4[\overline{DP} - (X+1)] - X} \times 100 \quad (4) \end{aligned}$$

It is seen from the data in Table 4 that the higher the \overline{DP} the higher the branching. This may be explained by the polycondensation mechanism in which the larger the size of the growing polybenzyl chain the more potential sites are available for attack by the reactive species. When the same catalyst was used and the reaction temperature was varied the \overline{DP} increased with increasing temperature but at 160°C is dropped considerably. At that temperature the reaction was extremely fast and perhaps the rate of the termination step increased significantly and did not allow the polybenzyl chain to grow. Polymer branching was found to be greater at higher temperatures; for instance, samples PB7 and PB10 have similar \overline{DP} but branching is much higher in sample BP7, prepared at 160°C, than in sample PB10, prepared at 140°C. Of course, catalyst must have some control over branching as well since these two samples were synthesized by two different catalysts. The percentage of hydrogens on terminal benzy ls, collected in Table 4, were determined by two methods. The results in column 5 were estimated by ^1H n.m.r. whereas those in column 8 were calculated from a combination of ^1H n.m.r. and \overline{DP} . The agreement between the two methods is surprisingly very good.

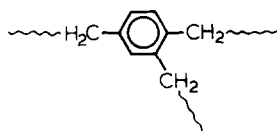
Although the ^1H n.m.r. spectra were not sufficiently well resolved to provide detailed information and insight about the type of polysubstitution which internal phenyl groups have undergone during polymerization, it is possible to make some predictions. From the theoretical point of view, the monosubstituted phenyl group shown below provides five different sites for electrophilic substitution.



However, the catalysts used in this study did not produce any *meta*-isomer (Table 2) and it might be safe to assume that *meta*-disubstituted phenyls were not formed in the polymerization as well. This leaves *ortho* and *para* positions as probable sites for attack generating the *ortho*- and *para*-disubstituted benzene rings.



If any trisubstitution occurs in polybenzyl chains, the *para*-disubstituted phenyl groups will provide one of the four equivalent positions for attack. However, in the *ortho*-disubstituted benzene rings, positions 4 and 5 are the most favourable for substitution relative to the other two positions because of less steric hindrance. Therefore, the most probable trisubstituted polybenzyl that will result from a disubstituted chain would have the structure shown below.



It is unlikely that any further substitution will occur on the backbone of a trisubstituted polybenzyl chain due to steric effects. Nevertheless, we are currently investigating the multisubstitution pattern of these polybenzy ls by ^{13}C n.m.r., the results of which will appear in a later publication.

Mechanism

It was shown^{13,14} previously in the Friedel-Crafts alkylation and acylation reactions catalysed by $\text{ArMo}(\text{CO})_3$ (Ar: toluene, polystyrene) that a cationic and not a free radical process was involved. Furthermore, it was shown that the active form of the catalyst retains the arene ring and that any free or exchanged $\text{Mo}(\text{CO})_3$ groups are present only in negligible amounts.

In this work, we chose to investigate the catalytic properties of several arene chromium tricarbonyls for the polymerization of benzyl chloride because of their high thermal stability relative to molybdenum and tungsten counterparts. From the mechanistic point of view, our intention was to attempt to elucidate factors which might provide additional information as to whether the arene ring remains attached to the metal throughout the course of the catalysis or dissociates first from the arene ligand before it can participate in the initiation step of the polymerization. Additional evidence that the arene is linked to the metal during the course of the reaction is provided by the following experimental observations. First, in Figure 1 the amount of HCl gas evolved (mmol) as a function of time is shown, for a series of substituted arene chromium tricarbonyl catalysts for the polymerization of benzyl chloride at constant temperature. The observed induction period and reaction rates varied among the catalysts employed at the same conditions. If the $\text{Cr}(\text{CO})_3$ group dissociates completely from the arene, only the length of the induction time should be affected by the nature of arene and not the reaction rates. Secondly, we allowed 15 ml toluene to reflux with 1.5 mmol of aniline chromium tricarbonyl for 2 h prior to introduction of benzyl chloride, with the expectation that enough $\text{tolCr}(\text{CO})_3$ would be formed by ring exchange to catalyse the alkylation reaction. It appears that some degree of ring exchange occurs as evidenced by the formation of $\text{tolCr}(\text{CO})_3$ identified by i.r. spectroscopy. However, upon the addition of benzyl chloride, catalysis did not occur; instead, aniline $\text{Cr}(\text{CO})_3$ precipitated out, probably because the nitrogen complexes with the benzyl chloride forming an insoluble salt.

Therefore, there is strong evidence that the arene remains attached to the metal while catalysis takes place. The observed induction times probably result from the time required for the arene ligand to dissociate partially, creating a metal vacant site so the benzyl chloride can coordinate. It is also possible that through oxidative addition the $\text{ArCr}(\text{CO})_3$ can lose a CO molecule to produce the $\text{ArCr}(\text{PhCH}_2)(\text{Cl})(\text{CO})_2$ catalytic species. A similar compound has been isolated when benzene chromium tricarbonyl was allowed to react with trichlorosilane¹⁹. Another way by which $\text{ArCr}(\text{CO})_3$ can become coordinatively unsaturated is to lose one or more CO groups. However, studies have shown²⁰⁻²² that $\text{ArM}(\text{CO})_3$ compounds lose CO only under u.v. radiation; therefore, this possibility may be ruled out since our reactions were conducted thermally. Hence, once the benzyl chloride is coordinated to the metal the reaction

may be of the usual Friedel–Crafts step-growth polymerization. It is unlikely, at least in the early stages of the polymerization, that any ring exchange occurs between the coordinated arene and the monomer since the chloromethyl group deactivates the ring inductively and makes it less basic than the already coordinated arene on the metal.

CONCLUSION

Although the $\text{ArCr}(\text{CO})_3$ homogeneous catalysts are milder and more selective than the conventional Lewis acid catalysts of the AlCl_3 type, it still appears impossible to polycondense benzyl chloride to a linear *para*-substituted, high molecular weight polymer. This failure may be attributed to the nature of the polybenzyl chain which as it grows generates more potential sites for attack by the reactive electrophilic species, the resulting polymer having a highly multisubstituted branch structure. To force these reactive species to attack the tail of the growing polybenzyl chain selectively rather than the backbone, one would require to jail and tie the catalyst inside the cavity of a polymeric matrix. This will make the system undergo catalysis inside the channels of the polymeric catalyst support. Because of steric hindrance, the active sites on the backbone of the polybenzyl chain may be frozen out, allowing the condensation reaction to take place on the tail of the growing chain in a linear fashion. These thoughts, however, are speculative and must await future experimental results.

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