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Polycondensation of benzyl chloride over Ga- and In-modified ZSM-5 type zeolites and Si-MCM-41 or Montmorillonite-K10 supported GaCl₃ and InCl₃ catalysts

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Abstract

Performance of In- and Ga-modified ZSM-5 type zeolites (namely, In₂O₃/H-ZSM-5, Ga₂O₃/H-ZSM-5, H-GaMFI and H-GaAlMFI) and InCl₃ or GaCl₃ supported on high silica mesoporous MCM-41 or on Mont.-K10 in the liquid phase polycondensation of benzyl chloride to polybenzyl has been investigated. Influence of solvent (namely, dichloroethane, *n*-heptane and ethanol) and temperature on the rate of polycondensation of benzyl chloride over the catalyst (InCl₃/Si-MCM-41) showing highest polycondensation activity has also been studied. The In- and Ga-containing solid catalysts show good or high activity in the polycondensation reaction at the reaction condition normally employed in the benzylation of aromatic compounds by benzyl chloride. However, the polycondensation is strongly influenced by the solubility of the polybenzyl polymer in the reaction medium and consequently by the solvent used as the reaction medium. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Benzylation of aromatic compounds, using homogeneous acid catalyst is a commonly practiced Friedel–Crafts type reaction in organic synthesis [1]. However, the commonly used homogeneous acid catalysts (e.g. AlCl₃, BF₃ and H₂SO₄, etc.) pose several problems, such as difficulty in recovery and/or separation, disposal of spent catalyst, corrosion, high toxicity, etc. Hence, development of a reusable solid catalyst having high activity in the Friedel–Crafts reactions is, therefore, of great practical importance.

The use of a number of solid catalysts, such as modified clays [2–8], heteropoly acids [10–12], metal containing MCM-41 [9,13,14] and HY, H-beta, H-ZSM-5 [15] and Fe- or Ga-substituted H-ZSM-5 [16] and Ga- or In-modified H-ZSM-5 [17] has been reported earlier for the benzylation with benzyl halide of benzene and other aromatic compounds.

Among the different benzyl halides (e.g. benzyl chloride, bromide or iodide), benzyl chloride is a commonly used benzylating agent for the benzylation of aromatic compounds. However, in the presence of many Lewis acid catalysts, benzyl chloride undergoes a self-condensation reaction to form polybenzyl [(*n* + 1)C₆H₅CH₂ClC₆H₅CH₂(C₆H₄CH₂)_{*n*}Cl + *n*HCl], which can be a predominant side reaction in the benzylation of aromatic compounds. It is therefore

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interesting to study the polycondensation of benzyl chloride over the solid catalysts to be used in the benzylation reactions. Earlier studies reported on the polycondensation of benzyl chloride are based on the use of homogeneous stannic chloride catalyst [18,19] and heterogeneous catalysts, such as ferrous sulfate [20], iron oxide [21] and other Fe-containing solid catalysts [22].

In our earlier studies, we have reported very high activity of different Ga- and In-modified ZSM-5 type zeolite catalysts [16,17] and Si-MCM-41 or Mont.-K10 supported GaCl₃ and InCl₃ catalysts [9] in the benzylation of benzene by benzyl chloride. Since there is a high possibility of polycondensation of benzyl chloride during the benzylation reaction, it is practically important to have the knowledge of the polycondensation over these solid catalysts. The present investigation was, therefore, undertaken to examine the activity of the Ga- and In-containing solid catalysts for the polycondensation reaction. In addition, the effect of temperature and solvent on the polycondensation reaction over a selected catalyst has also been studied.

2. Experimental

Ga- and In-containing solid catalysts used in the polycondensation reactions are given in Table 1.

The ZSM-5 type zeolite catalysts: H-ZSM-5 (Si/Al = 30), H-GaMFI (Si/Ga = 33) and H-GaAlMFI (Si/Ga = 15.7, Si/Al = 46.8) were prepared and characterized by the procedure similar to that described earlier [16,23–25].

Ga₂O₃ (5%)/H-ZSM-5 (Si/Al = 30) and In₂O₃ (5%)/H-ZSM-5 (Si/Al = 30) catalysts were prepared and characterized by the procedure reported elsewhere [17].

GaCl₃ (10%)/Si-MCM-41 or Mont.-K10 and InCl₃ (10%)/Si-MCM-41 or Mont.-K10 catalysts were prepared by impregnating anhydrous metal chloride from its acetonitrile solution on high silica mesoporous MCM-41 (surface area = 1180 m² g⁻¹) or Mont.-K10 (obtained from Aldrich Chemicals, USA) by incipient wetness technique and evaporating the solvent in vacuum oven at 120°C for 8 h [9].

The polycondensation reaction was carried out in a magnetically stirred glass reactor (capacity = 25 cm³) fitted with a reflux condenser, having a low dead vol-

ume, mercury thermometer and arrangement for continuously bubbling moisture-free nitrogen (flow rate = 30 cm³ min⁻¹) through the liquid reaction mixture at the reaction conditions given in Table 1. The reaction was started by injecting benzyl chloride in the reaction mixture, containing a solvent and the catalyst at different reaction temperature. The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by nitrogen in a 0.1 M NaOH solution containing phenolphthalein indicator) as a function of time. The conversion data were corrected for a small time lag (1.1 min) between the evolution of HCl in the reaction and the analysis of the evolved HCl by titration. The time lag was determined experimentally by bubbling a HCl–N₂ gas mixture (30 cm³ min⁻¹) through the reaction mixture in the absence of benzyl chloride and detecting the HCl at the reactor outlet.

After completing the reaction, the polymer was dissolved in benzene, separated from the catalyst by filtration, washed with water, dried and finally poured into excess methanol. The precipitated polymer was collected, washed with methanol for several times and dried in vacuum oven at 60°C for 24 h. The purified polymer was used for the determination its thermal stability, NMR, elemental analysis and average molecular weight.

3. Results and discussion

3.1. Comparison of catalysts for polycondensation of benzyl chloride

Results on the polycondensation of benzyl chloride over the different Ga- and In-containing solid catalysts are presented in Table 1.

H-ZSM-5 zeolite (which is highly acidic) shows no activity in the polycondensation reaction, but its catalytic activity is increased drastically because of a partial or complete substitution of its framework Al by Ga or because of the impregnation of the H-ZSM-5 zeolite with Ga₂O₃ or In₂O₃. Among the Ga₂O₃/H-ZSM-5 and In₂O₃/H-ZSM-5 catalysts, the later showed higher catalytic activity in the polycondensation reaction. All the above observations are quite consistent with that observed earlier in the case of benzylation of benzene over these catalysts [16,17].

Table 1
Results of the polycondensation of benzyl chloride over different Ga- and In-containing solid catalysts^a

Catalysts	Acidity ^b (mmol g ⁻¹)	Solvent used in the reaction	Time (min) required for conversion of benzylchloride		Reaction induction period, <i>t</i> ₀ (min)	Apparent rate constant, <i>k</i> _a × 10 ³ (min ⁻¹)
			50%	90%		
H-ZSM-5	0.26	Dichloroethane	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h
Ga ₂ O ₃ (5%)/H-ZSM-5	0.18	Dichloroethane	18.0	32.0	1.6	112.4
In ₂ O ₃ (5%)/H-ZSM-5	0.23	Dichloroethane	12.5	25.0	1.0	135.4
H-GaMFI	0.29	Dichloroethane	37.0	88.0	7.3	33.9
H-GaAlMFI	0.44	Dichloroethane	26.0	66.0	5.5	42.6
Mont.-K10	–	Dichloroethane	5% conversion upto 1.5 h	5% conversion upto 1.5 h	5% conversion upto 1.5 h	5% conversion upto 1.5 h
GaCl ₃ (10%)/Mont.-K10	–	Dichloroethane	11.0	26.0	0.9	112.5
InCl ₃ (10%)/Mont.-K10	–	Dichloroethane	9.2	19.5	0.5	156.1
Si-MCM-41	–	Dichloroethane	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h
GaCl ₃ (10%)/Si-MCM-41	–	Dichloroethane	14.5	30.5	2.0	104.6
InCl ₃ (10%)/Si-MCM-41	–	Dichloroethane (at 80°C)	10.5	22.5	1.0	148.1
InCl ₃ (10%)/Si-MCM-41	–	<i>n</i> -Heptane (at 98°C)	181.0	–	2.5	4.1
InCl ₃ (10%)/Si-MCM-41	–	Ethanol (at 78°C)	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h	No conversion upto 1.5 h

^a Reaction conditions: reaction mixture = 1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst at different reaction temperature.

^b Acidity measured in terms of the pyridine chemisorbed at 400°C.

The high polycondensation activity of the Ga- and In-modified ZSM-5 type zeolite catalysts is attributed to the presence of non-framework Ga- or In-oxide species (which are added externally by impregnation or formed due to degallation of the framework Ga during their calcination/pretreatment) [24,25] in their channels and also on their external surface. It is interesting to note that the polycondensation reaction over the Ga- or In-modified ZSM-5 zeolite catalysts undergoing to completion (upto 100% conversion of benzyl chloride). This is not possible if the polycondensation would have occurred in the zeolite channels (which are small in diameter, 0.5–0.7 nm) because of the blockage of the channel by the polymer molecules formed in the initial reaction. At this reaction temperature (80°C), there is no possibility of the desorption of polymer molecules from the zeolite channel. Hence, the polycondensation reaction over the Ga- or In-modified H-ZSM-5 occurs essentially on the Ga-oxide or In-oxide present on external surface of the zeolite crystals.

Similarly, Mont.-K10, which is acidic shows very poor activity in the polycondensation reaction but the GaCl₃ or InCl₃ supported on the Mont.-K10 shows very high polycondensation activity.

Among the high silica mesoporous MCM-41 type catalysts, Si-MCM-41 (having no acidity) shows no polycondensation activity but the Si-MCM-41 supported GaCl₃ and InCl₃ catalysts show very high polycondensation activity.

The above results reveal that the acidity alone is not enough for a catalyst to be active in the polycondensation reaction. The observed high polycondensation activity of the Ga- or In-containing catalysts seems to be attributed to the redox properties of the gallium or indium species present in the catalyst. The polycondensation activity of Ga-, In- and Fe-containing catalysts (Table 2) is in the order same as that for their redox potential ($E_{\text{Ga}^{3+}/\text{Ga}}^0 (-0.53 \text{ V}) < E_{\text{In}^{3+}/\text{In}}^0 (-0.34 \text{ V}) < E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 (+0.77 \text{ V})$).

The In-containing ZSM-5, Mont.-K10 and MCM-41 catalysts show higher polycondensation activity as compared to the Ga-containing solid catalysts. Further, a comparison of the Ga- and In-containing solid catalysts with the corresponding Fe-containing solid catalysts [22] for their polycondensation activity in Table 2 shows that the Fe-containing cata-

lysts are more active than the corresponding Ga- or In-containing catalysts. This is consistent with the earlier observations that the selectivity in the benzylation of benzene to diphenylmethane over the Ga- and In-containing solid catalysts was higher than that of the Fe-containing solid catalysts [9,17].

3.2. Effect of solvent on polycondensation

In order to study the effect of solvent on the rate of polycondensation of benzyl chloride over InCl₃ (10%)/Si-MCM-41 catalyst, the reaction was carried out using different solvent (namely, dichloroethane, *n*-heptane and ethanol) under reflux. Among the different solvents used, the reaction rate in dichloroethane is much higher whereas, in case of *n*-heptane and ethanol as a solvent, it is very slow and almost zero, respectively (Table 1). This is expected mostly because of the high solubility of the polymer in dichloroethane and little or no solubility of the polymer in the other solvents. When the solubility of the polymer in a particular solvent is low, the polybenzyl formed on the catalyst surface is not removed from the surface and this is expected to deactivate the catalyst due to occupation of its active sites by the product formed during the initial reaction.

3.3. Kinetics and mechanism of polycondensation reaction

Analysis of the results of the evolution of hydrogen chloride indicates that the polycondensation of benzyl chloride over these solid catalysts follows first-order rate law (with respect to benzyl chloride conversion),

$$\log \left[\frac{1}{1-x} \right] = \left(\frac{k_a}{2.303} \right) (t - t_0) \quad (1)$$

where x is the fractional conversion of benzyl chloride, measured in terms of the HCl evolved in the reaction, k_a the apparent first-order rate constant, t the reaction time and t_0 the reaction induction period. A plot of $\log [1/(1-x)]$ against $(t - t_0)$ is linear over a wide range of benzyl chloride conversion (10–90%). It was also observed in most of the earlier studies that the initial portion (upto 10%) of the kinetic plot is not linear and the plot does not pass through the origin [18,19].

Table 2

Comparison of Ga- and In-containing solid catalysts with the corresponding Fe-containing catalysts [22] for their polycondensation activity (at 80°C) under identical reaction conditions^a

Catalyst	Apparent rate constant, $k_a \times 10^3 \text{ (min}^{-1}\text{)}$	Reference
H-GaMFI	33.9	Present
H-FeMFI	112.9	[22]
Ga ₂ O ₃ (5%)/H-ZSM-5	112.4	Present
In ₂ O ₃ (5%)/H-ZSM-5	135.4	Present
Fe ₂ O ₃ (5%)/H-ZSM-5	348.9	[22]
GaCl ₃ (10%)/Mont.-K10	112.5	Present
InCl ₃ (10%)/Mont.-K10	156.1	Present
FeCl ₃ (10%)/Mont.-K10	180.0	[22]

^a Reaction mixture = 1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst.

The effect of temperature on the rate of polycondensation reaction over InCl₃ (10%)/Si-MCM-41 catalyst (which showed highest polycondensation activity among the catalysts) was studied by conducting the reaction at 60, 70 and 80°C under similar conditions. The kinetic curves at different temperatures are shown in Fig. 1. The apparent first-order rate constants (k_a)

at the different temperatures are given in Table 3. A linear temperature dependence, according to the Arrhenius equation, for the polycondensation reaction is shown in Fig. 2. The Arrhenius parameters (activation energy and frequency factor) for the polycondensation reaction, estimated from the linear Arrhenius plot for the reaction are included in Table 3.

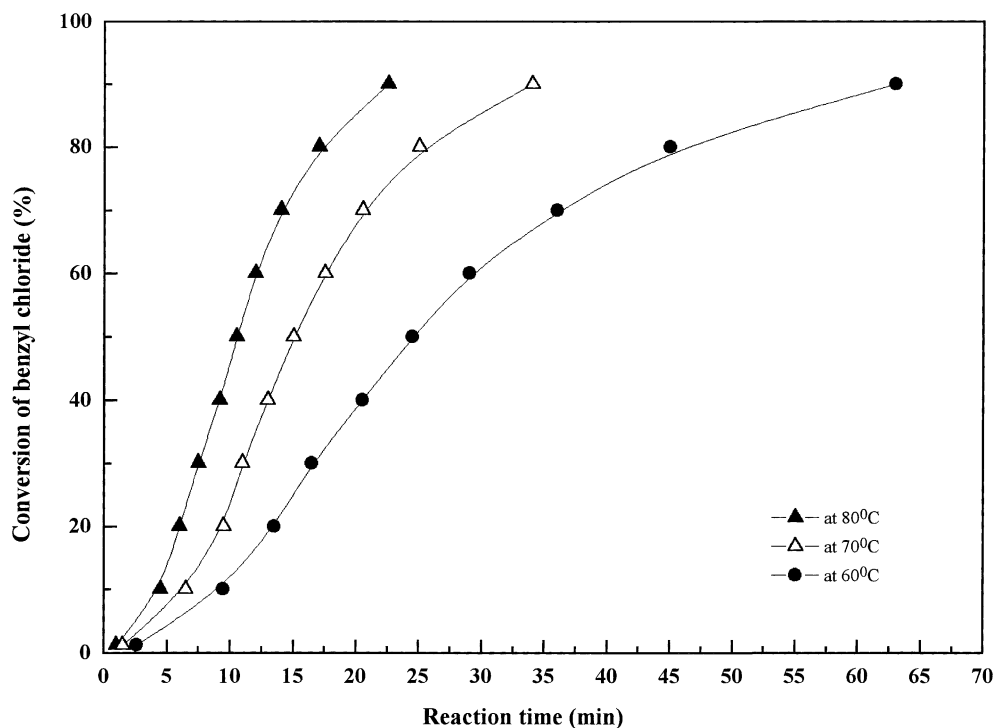


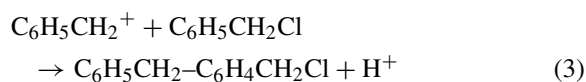
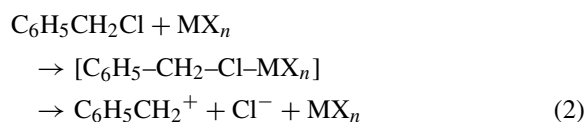
Fig. 1. Effect of reaction temperature on the conversion of benzyl chloride in the polycondensation reaction over InCl₃ (10%)/Si-MCM-41 catalyst.

Table 3
Kinetic parameters for the polycondensation of benzyl chloride over InCl_3 (10%)/Si-MCM-41 catalyst^a

Apparent rate constant, $k_a \times 10^3$ (min^{-1})			Activation energy, E (kcal mol^{-1})	Frequency factor, A (min^{-1})
60°C	70°C	80°C		
46.2	87.0	148.1	7.45	6.07×10^3

^a Reaction conditions: dichloroethane/benzyl chloride mole ratio = 18.5, catalyst/benzyl chloride wt. ratio = 0.1, volume of the reaction mixture = 14 ml and N_2 flow rate = 30 ml min^{-1} .

The polycondensation of benzyl chloride is a typical Friedel–Crafts reaction. The primary step in the polycondensation reaction seems to be the generation of stable benzyl carbonium ion, which attacks another molecule of benzyl chloride to form a dimer, as follows:



where $M = \text{Ga}$ or In and $X = \text{O}$ or Cl and n is the no. of atoms of X needed to fulfil the valence requirement of M .

Once the dimer is formed, there is a competition between the dimer and the benzyl chloride to be attacked by the benzyl carbocation. Earlier studies [26] showed that the presence of chlorine atom in benzyl chloride reduces its reactivity, but its effect on dimer, trimer or higher polymer is small and because of this, the reactivity of polymer is assumed to be much greater than benzyl chloride. Hence, the reaction proceeds to form polymer rather than leading to simple dimerisation. The conversion versus time curves (Fig. 1), showing an exponential

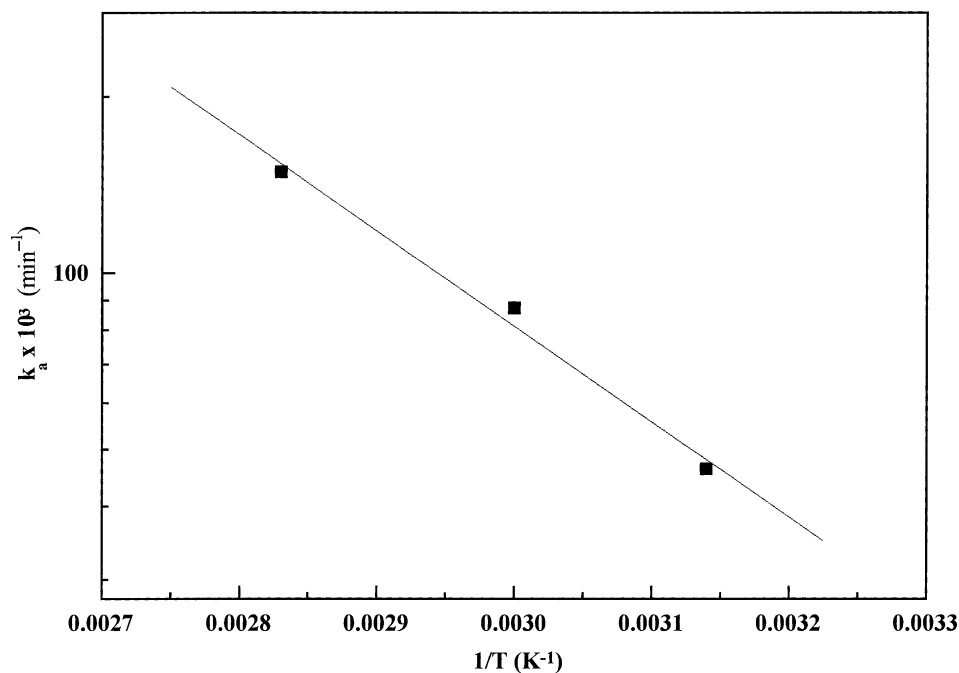


Fig. 2. Arrhenius plot of $\log k_a$ against $1/T$ for the polycondensation of benzyl chloride over InCl_3 (10%)/Si-MCM-41 catalyst.

increase in the conversion at lower reaction period (an auto-catalytic type nature) is consistent with the above.

3.4. Reaction induction period

Induction period for the polycondensation (Table 1) has been estimated from the intercept on the time axis of the benzyl chloride conversion versus time curve extrapolated to the zero conversion. The kinetic curve (Fig. 1) shows that the induction period increases with decreasing the reaction temperature. The observed induction period may be attributed to the formation of

the active complex between the catalyst and reactants; the time required for its formation at higher temperature is shorter than that at lower temperature. It may also be due to a lower reactivity of benzyl chloride as compared to its dimer or higher polymer. It may be noted that even in the homogeneously catalyzed polycondensation reaction of benzyl chloride [18], an induction period was observed. Our earlier studies of the benzene benzylation by benzyl chloride over these catalysts [9,27] revealed that the reaction induction period depends strongly on the moisture-content of the reaction mixture; it is increasing with increasing the moisture content and vice versa. Further work

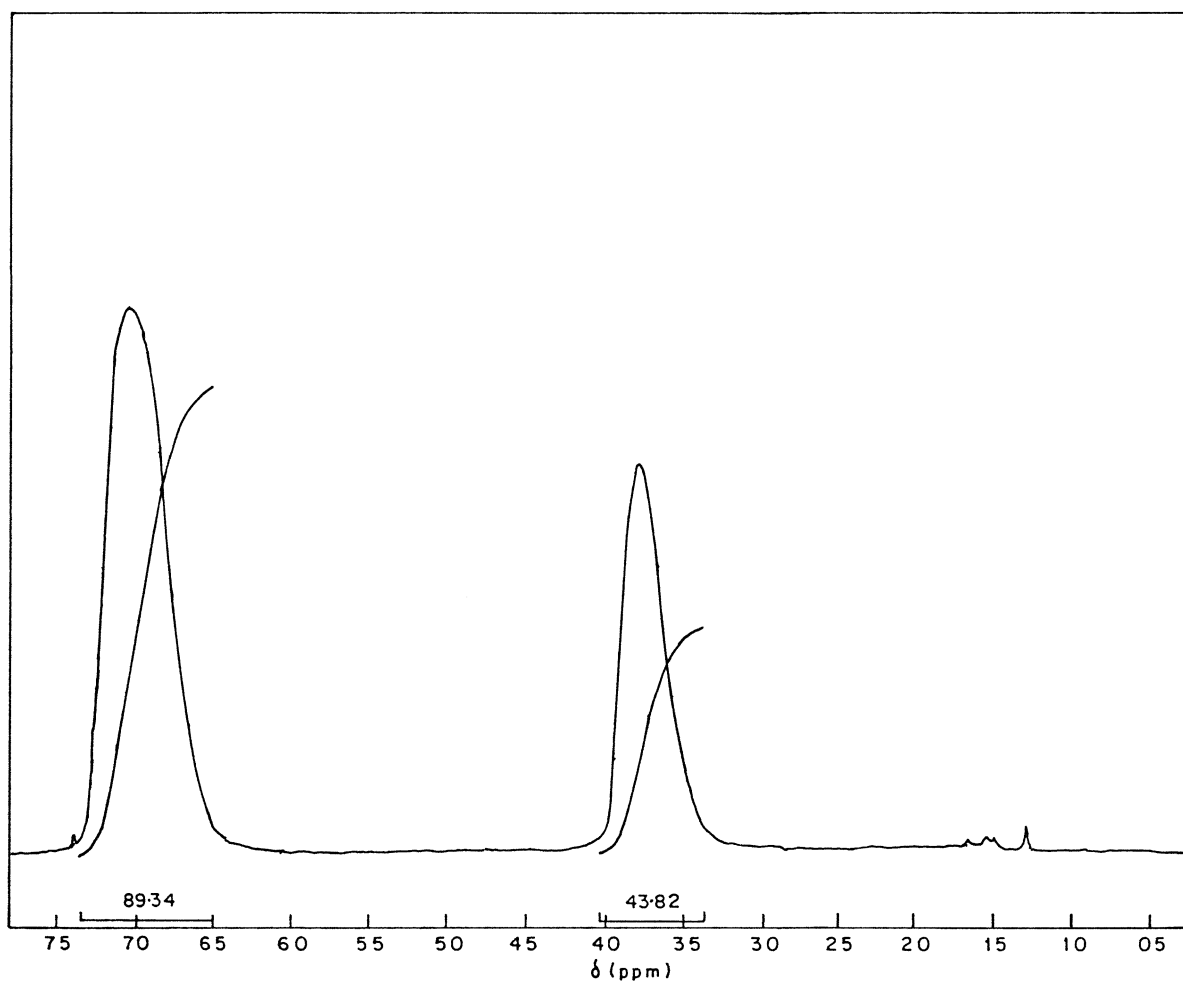


Fig. 3. NMR spectrum of the polycondensation product.

is necessary for a clear understanding of the exact cause of the induction period in the polycondensation.

3.5. Characterization of polymer

The polymer NMR (Fig. 3) shows two broad singlets (δ : 7.0 (4H, phenylene H) and 3.8 (2H, CH₂)). The elemental analysis showed that the polymer contains 6.6–6.7% hydrogen, 93.1–93.3% carbon and only a trace amounts (below detectable levels) of chlorine. The elemental analysis and NMR spectra of the polymer clearly show that the polymer formed in the polycondensation is predominantly linear *para*-substituted polybenzyl. The average molecular weight (measured by the vapour pressure osmometry using benzene at 28°C) of the polymer was found to be 4400 ± 100. The polymer is also characterized by TG-DTA analysis in air, which shows that the polymer is thermally stable upto 420°C above which it starts decomposing. The polymer is decomposed completely at 705°C.

4. Conclusions

This work led to the following important conclusions.

1. The modification of H-ZSM-5 by completely or partially substituting its framework Al by Ga or by depositing on it Ga₂O₃ or In₂O₃ results in a drastic increase in its benzyl chloride polycondensation activity. Among the Ga- and In-containing solid catalysts, the Ga₂O₃ (or In₂O₃)/H-ZSM-5, GaCl₃/Si-MCM-41 (or Mont.-K10) and InCl₃/Si-MCM-41 (or Mont.-K10) catalysts showed very high polycondensation activity; the InCl₃/Si-MCM-41 (or Mont.-K10) showed the highest activity. However, these catalysts are less active than the corresponding Fe-containing catalysts for the polycondensation and hence are more selective for the benzylation of aromatic compounds by benzyl chloride.
2. The polycondensation reaction over all the In- and Ga-containing catalysts follows first-order kinetics, valid for the benzyl chloride conversion in the range of 10–90%.

3. For the polycondensation reaction over InCl₃ (10%)/Si-MCM-41, the activation energy and frequency factor are found to be 7.45 kcal mol⁻¹ and 6.07 × 10³ min⁻¹, respectively.
4. The solvent used as a reaction medium plays an important role in the polycondensation. The reaction rate in the different solvents is in the following order: dichloroethane ≫ *n*-heptane ≫ ethanol, which is same as the order for the solubility of the polymer in the solvents.

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