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ANIONIC POLYMERIZATION WITH COMPLEX BASE. I. POLYMERIZATION OF PHENYLISOCYANATE

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ABSTRACT

In this work, phenylisocyanate was polymerized in bulk and in a solution of THF by the complex base (CB), $NaNH_2/(CH_3)_3CONa$ catalyst under vacuum. The percent yield for bulk polymerization at –20°C first increased with a slow rate reaching 32% conversion in 3 hours, then with a greater rate up to 86% in 6 hours. However, at 0°C the yields were relatively smaller and not very reproducible. The product obtained was a high molecular weight polymer, insoluble in most solvents, and partially crystalline. The polymerization in THF at –20° gave 58% conversion in 9 hours with a high rate first, then a slower rate. The polymer samples were characterized by fractionation, FT-IR, DSC, NMR, TGA, and X-ray powder diffraction. The polymer samples in the solution polymerization contained trimer and oligomeric components. No glass transition temperature was observed at the temperature interval studied.

Key Words: Monoisocyanade; Complex base; Ionic polymerization; Sodium amide; Sodium isobutoxide

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INTRODUCTION

Organometallic, as well as metals such sodium and potassium, are well known as initiators for anionic polymerization. Moreover, in order to increase or modulate the reactivity of these classical initiators, the influence of additives such as tertiary amine [1], linear and macrocyclic polyethers [2–3], various alcohol [4] and alkali alkoxides [5–6] has been subject of many works. Raynal *et al.* [7] prepared the reagent $NaNH_2$-RONa called Complex Base (CB). RONa, which is called an activating agent, can be an alkoxide or a ketone enolate. The catalyst has different properties from each of the $NaNH_2$ and RONa. It is even highly active in weakly polar solvents such as THF or benzene. Thus, it might be expected that an enhanced reactivity of the amide anion was used for polymerization. The CB has been used in polymerization of various monomers [8–9]. CB is simply prepared by the addition of an alcohol to a calculated excess amount of $NaNH_2$. The main factors influencing their reactivity are the ratio of $NaNH_2$/RONa, the nature of the solvent, and the activating agent.

Poly(monoisocyanate), also known as nylon-1, shows very useful properties such as liquid crystals [10]. Therefore, the polymerization of monoisacyanate has received much attention, but the mechanism of the reaction is not fully understood. The effect of the different initiator and polymerization conditions lead mostly to controversial results. The polymerization of several monoisocyanates was first reported by Shashoua *et al*. [11]. They noted that free-radical, metal alkyls, sodamide, or Grignard reagent initiators can be used for polymerization. Since, monoisocyanates are very reactive, different side products can also be produced. The most important of these is cyclization mostly trimerization). Natta *et al.* [12] polymerized phenyl isocayanate using ethyllithium in toluene. Transition metal catalysts at a low temperature of – 45°C produced low conversion to the polymer, and when the temperature was raised to room temperature, the main product was a trimer [13]. Sobur *et al.* [14] polymerized phenylisocyanate by γ-radiation at 20, –78, and –196°C in bulk and in DMF. In recent years, a different catalyst system has been studied in polymerization of phenylisocyanate [15–19]. Poly(phenylisocyanate), PPIC, is not soluble in most known solvents, except dissolution by degradation to a trimer in concentrated sulfuric acid. Since the polymers are usually living types, they undergo several rearrangement reactions by back-biting, depolymerization, etc. Therefore, when polymerized with a strong base or high concentration of initiator, the products are usually dimer, trimer, cyclic, or linear oligomers. The complex base catalyst, $(NaNH_2)_m/((CH_3)_3CONa)_n$ can be prepared for a different ratio of m/n to give base strength that is most suitable for polymerization. The polymer obtained is characterized by different methods to gain information about the polymerization mechanism and polymer structure.

EXPERIMENTAL

Chemicals and Instruments

30% $NaNH_2$ suspension in xylene (Fluka), spectroscopic grade methanol (Merck), acetic acid (Merck), spectroscopic grade acetone (Merck) and spectroscopic grade t-butanol (Merck) were used without further purification. THF (Merck) was kept on CaH_2 overnight, then distilled in vacuum over sodium mirror. Toluene (Merck) was purified by first keeping it over CaH_2 powder overnight, then distilled under vacuum onto sodium mirror.

FT-IR spectra of monomer and polymer samples were taken on a Nicolet FT-510 model FT-IR spectrophotometer using KBr pellets. Proton and ^{13}C-NMR spectra of samples in deutoriated acetone were taken on a Bruker GmbH DPX, 400 MHz high performance FT-NMR spectrometer. X-ray powder spectra of samples were taken on a Huber-Guinier G600 powder diffractometer on a Enraf-Nonius 551-Model Generator (CuKα radiation, 15 mA and 35 kV). DSC thermograms were taken on a TA 2000 DuPont Instrument 910S DSC with a heating rate of 10°C/min. TGA thermograms were taken on a TA 2000 DuPont Instrument 951 TGA with a heating rate of 10°C/min.

Procedure

Synthesis of Complex Base (CB)

A solution of $(CH_3)_3COH$ in toluene was added dropwise to a suspension of $NaNH_2$ in toluene at room temperature. After the evolution of NH_3 gas was completed, the mixture was heated for about 2 hours at 45–50°C to almost dryness. If completely dried, it loses its activity. A known amount of CB was placed in a flask, which was equipped, with a condenser and separator funnel containing water. The other end of condenser was connected to a flask containing known amount of standard HCl solution. When water was added slowly to CB, the $NaNH_2$ in the complex mixture of $(NaNH_2)_m((CH_3)_3CONa)_n$ changed to NH_3 and distilled into standard HCl solution.

$$NaNH_2 + H_2O \rightarrow NH_3(g) + NaOH$$

The excess HCl was titrated with standard NaOH solution and difference gives the moles of NH_3 distilled, which is also the mol of $NaNH_2$. Titration of base in the first flask with standard HCl solution gives the total mol of NaOH produced in above reaction and $(CH_3)_3CONa$. Thus, the mol ratio of $NaNH_2$: $(CH_3)_3CONa$ is calculated from the titration data.

Bulk and Solution Polymerization

In bulk polymerization, a desired amount of complex base (CB) was taken into reaction tube. It was connected to the vacuum system and the solvent of the

CB was pumped out under vacuum at room temperature. Then, a desired amount of monomer was transferred into a catalyst mixture by vacuum distillation. The reaction tube was then cut by flame sealing and transferred into the constant temperature (-20°C and 0°C) bath prepared for the polymerization reaction. After the desired polymerization time, the sealed end of reaction tube was brake opened to the atmosphere and excess amount of methanol containing acetic acid (ratio of 4:1) was added to terminate polymerization reaction. The insoluble polymer fraction was separated by filtration and dried to constant weight. The best results were obtained for the ratio of m:n of 1:1 in the complex base $(NaNH_2)_m((CH_3)_3CONa)_n$.

Solution polymerization was carried out similar to the bulk polymerization, but in this case the catalyst and monomer were placed into THF as a solvent before mixing. Polymerization was repeated with $NaNH_2$, $(CH_3)_3ONa$ and their complex (CB) as catalysts. Polymers obtained in both bulk and solution polymerization were extracted with several common solvents to separate dimer, trimer, oligomers, and different polymer fractions. Each were identified and characterized to understand the mechanism of polymerization better.

RESULTS AND DISCUSSION

Anionic Polymerization of Phenylisocyanate

The time and conversion for bulk polymerization at –20°C and 0°C are given in Table 1. At –20°C, the conversion increases steadily up to 32% in 3 hours, then accelerates more and reaches a value of 86% in 6 hours. At 0°C, the change of conversion with polymerization time is not much different then that at –20°C. However, the conversions at 0°C were not precisely reproducible. No explanation could be given for this behavior.

The results for solution polymerization at –20°C under vacuum are given in Table 2. Since, the results of 0°C polymerization were even less precisely reproducible compared to bulk polymerization, they are not given. Further work will be done to find a reasonable explanation. When compared to bulk polymerization,

Table 1. Bulk Polymerization of Phenylisocyanate under Vacuum with CB

Time (h)	Temperature (°C)	% Conversion
0.50	20	21
1.00	20	22
3.00	20	32
6.00	20	86
0.50	0	22
1.00	0	29
4.67	0	45

Table 2. Solution Polymerization of Phenylisocyanate under Vacuum at –20°C with CB

Time (h)	% Conversion
1.00	19
2.00	27
3.00	44
6.00	46
9.00	58

the conversion values are lower and the rate of polymerization increased more slowly at a higher reaction time.

In the case of bulk polymerization, there was no solid residue obtained when methanol from the polymer filtrate was evaporated to dryness. However, in the case of solution polymerization, a residual solid was obtained at a lower reaction time with a decreasing amount up to 3 hours of polymerization time, then none was observed. The analysis showed them to be cyclic or linear oligomers.

When $(CH_3)_3CONa$ was used as an initiator in the bulk polymerization of phenylisocyanate under vacuum and at –20°C, the conversion was 32% after 6 hours. However, no polymer was obtained in bulk or solution polymerization when $NaNH_2$ was used as an initiator. This is most probably due to the high base strength of $NaNH_2$, that depolymerization of poly(phenylisocyanate) is predominate to its polymerization under much more basic conditions, and/or the insolubility of the initiator in monomer and solvent. Thus, the complex base catalyst gives the best basicity condition for the anionic polymerization of monoisocyanate.

Characterization by Infrared

The FT-IR spectrum of monomer is given in Figure 1, and that of the polymer samples obtained in bulk polymerization at –20°C and 0°C, and in solution polymerization at –20°C are given in Figure 2. The most characteristic peak of the monomer (Figure 1) is the isocyanate peak at about 2300 cm^{-1}. The peaks corresponding to the phenyl group are at 3067, 3031, 1599, and 1457 cm^{-1}. The other peaks in the monomer spectrum correspond to C=N, C-N and substituted phenyl groups. They are sharp peaks, indicating a regular monomer structure, which are mostly of sp^2- hybridization, planar structure, and not many vibrational movements. The FT-IR spectra of polymers obtained at different polymerization times are the same. In all polymer samples spectra, the isocayanate (-N=C=O) peak around 2300 cm^{-1} disappeared, and no peaks are observed in the 2000–4000 cm^{-1}range. Therefore, the extended spectra in the range of 400–2200 cm^{-1} (Figure 2) for the polymer samples are shown. In the polymer FT-IR spectrum, a new intense peak at 1720 cm^{-1} shows the formation of amide linkages. This confirmed that the monomer addition took place through N=C bond, resulting in a polyamide chain.

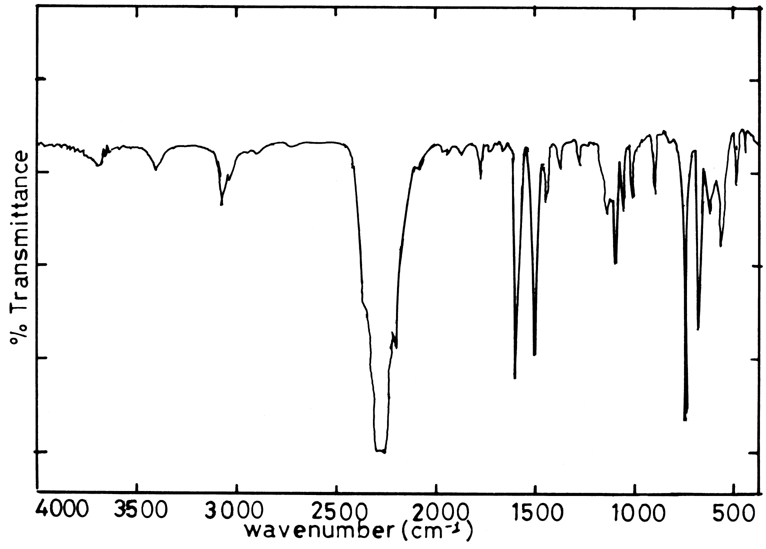


Figure 1. FT-IR spectrum of phenylisocyanate.

The peaks at around 1593, 1493, and 1456 cm^{-1} correspond to aromatic C-C stretching in the ring. They are the same peaks observed in the monomer spectrum, but have some shifts in their positions and relative peak intensities. Broad peaks around 1278–1320 cm^{-1} show a C_6H_5-NH group present at chain end. The peak at 1260 cm^{-1} shows the interaction between N-H bending and C-N stretching. The broad peak at 1175–1157 cm^{-1} represent C-N stretching in NH_2-C=O group. The presence of this group indicate that polymerization is initiated by NH_2^- of $NaNH_2$, which should be at one end of the polymer chain. The broad peak with splitting at 753, 722, and 690 cm^{-1} are assigned to N-H wagging for the C_6H_5-N-H. The general spectral shape of different polymer samples are the same. The difference is in peak shape and/or relative intensities of peaks. This shows some structural differences in the samples obtained under different conditions. The absence of etheric peak at about 1100 cm^{-1} in the spectra of polymer samples show that the monomer addition reactions are not via the C=O bond addition. Thus, products are polyamide, but not polyether.

In order to identify the presence of trimer, the IR of trimer (phenylisocyanurate) prepared by the method described previously [20] was taken. No difference could be obtained from the difference of the FT-IR spectra of the polymer and the trimer for phenylisocyanate. However, the peaks are sharper in the pure trimer spectrum, which could not be separated from the broad peaks of polymer in a mixture. Similar FT-IR spectral results are also reported [21] for poly(n-butylisocyanate) and its trimer. Therefore, it is not possible to distingush polymer and trimer from the IR spectra.

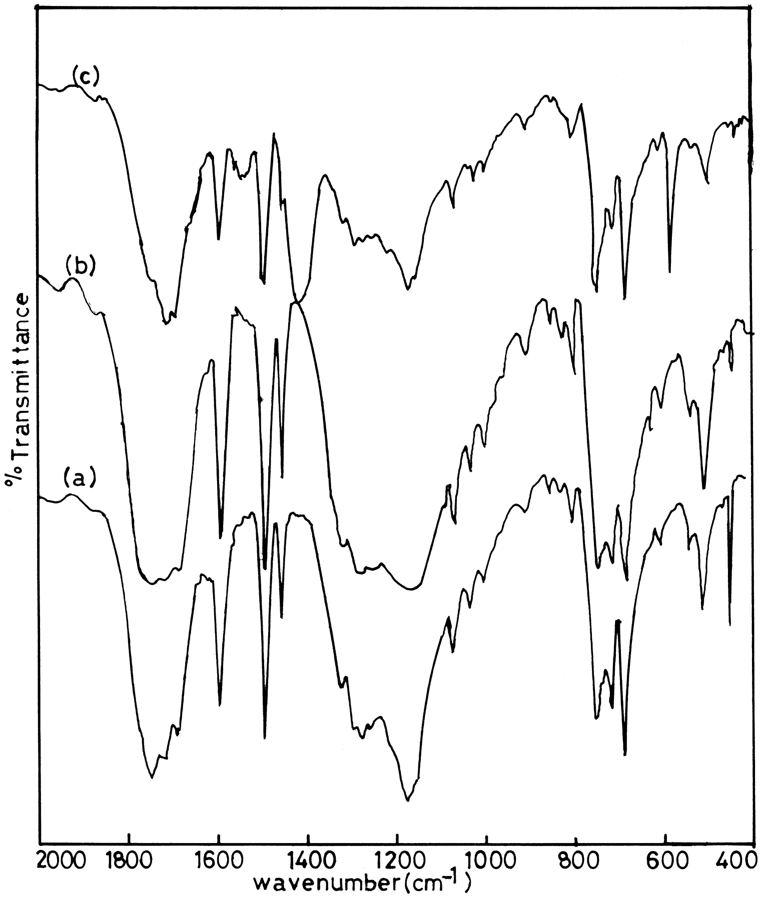
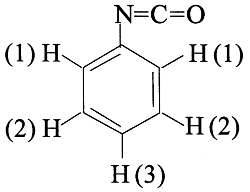


Figure 2. FT-IR spectrum of polymer obtained at (a) –20°C in bulk, (b) 0°C in bulk, and (c) –20°C in solution.

Characterization by NMR

Proton and ^{13}C- NMR spectra of monomer, trimer, and polymer were taken to characterize different products obtained in the polymerization process. The ^{1}H-NMR spectra of monomer, trimer and polymer are shown in Figure 3. The proton assignment to monomer are given in the following formula:



Since all the protons are on the benzene ring, the peak corresponding to this ring is about 7 ppm. Therefore, the extended spectrum of samples between 7 to 7.6 ppm are shown in Figure 3. The calculated chemical shift [22] for H (1) and H (2) are 7.13 ppm and 7.23 ppm, respectively. From the structure, it is expected that H (1) will give a doublet, H (2) and H (3) triplet or multiplet. In the monomer spectrum of (Figure 3a) the doublet at 7.20–7.22 ppm most probably corresponds to H (1). The other peaks, if interpreted as two triplet should be H (2) at 7.37–7.41 ppm and H (3) at 7.24–7.27 ppm. The number of each of H (1) and H (2) are two, but that of H (3) is one. Therefore, the intensity of H (1) and H (2) peaks should be equal to each other and twice that of H (3).

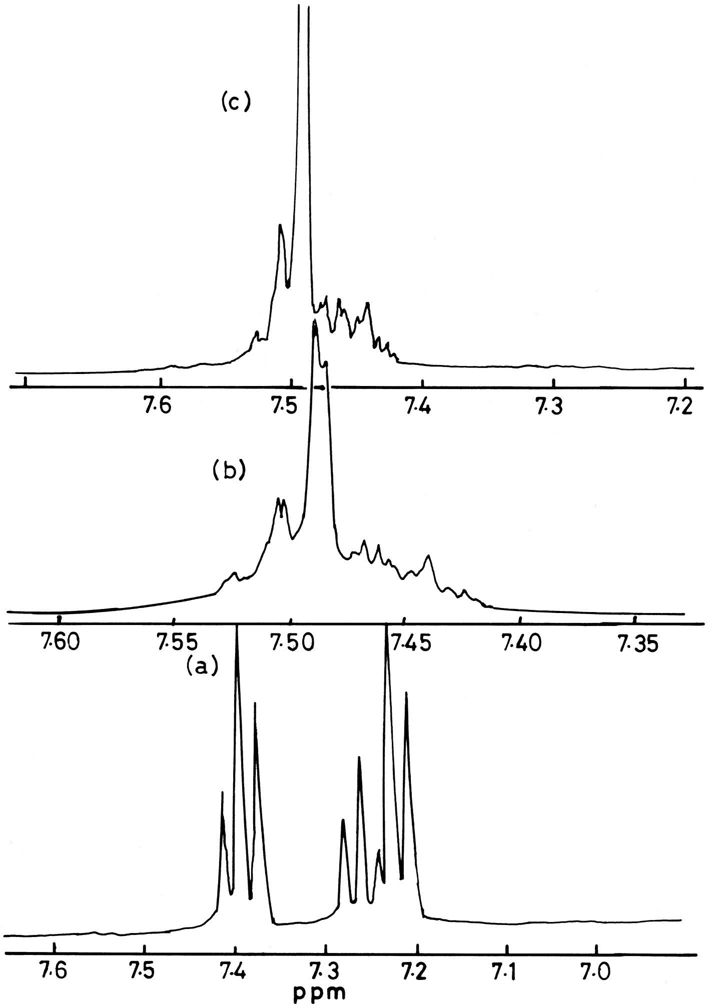
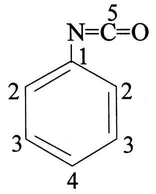


Figure 3. ^{1}H- NMR spectrum of (a) monomer, (b) trimer, and (c) polymer obtained by solution polymerization.

The ^{1}H-NMR spectrum of phenylisocyanurate (trimer) is shown in Figure 3b. In this spectrum peaks are observed in the range of 7.4–7.6 ppm. The assignment of H-number is the same as that of the monomer. There are important changes in peak positions and shape when compared to that in the monomer. The peaks become broader and more splitting is observed. The peak overlapping makes the assignment to protons difficult. The ^{1}H-NMR spectrum of polymer obtained from solution and bulk polymerization are quite similar. Not many differences were also observed when the samples were fractionated; the spectrum of a polymer sample is shown in Figure 3c. The peaks are in the range of 7.3–7.6 ppm. They are different from that of monomer and trimer with respect to peak shapes. The peaks are broader and there is too much overlapping. This might be due to the complex nature of the product.

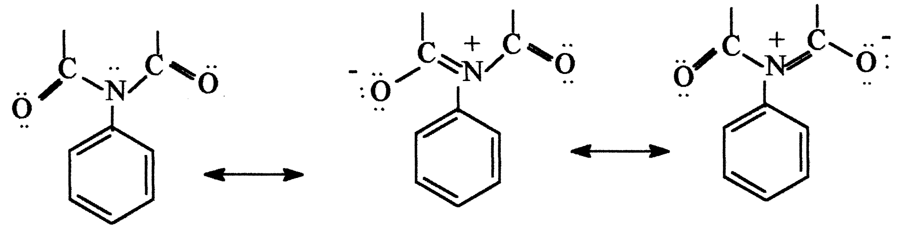
^{13}C-NMR spectra of monomer, polymer, and trimer are given in Figure 4. The peaks for monomers are observed in the range of 125–134 ppm. The assignment of numbers to each carbon in the monomer molecule is as follows:



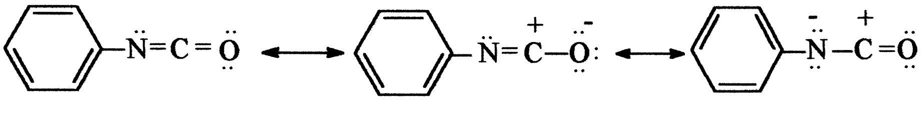
The assigned numbers to each carbon in trimer and polymer are also similar to that of the monomer. The observed and calculated [23] chemical shifts are tabulated in Table 3.

It is known that, the chemical shift increases with the decrease of electron density around the nucleus (and H atoms) by electron-withdrawing groups (deshielding). Hence, the electron-withdrawing capability of the tricoordinated nitrogen atom placed in between two electron-withdrawing carbonyl groups in the structure of trimer would be higher than that of the dicoordinated N-atom of the monomer. The following possible resonance structures of trimer and monomer, respectively support this suggestion:

Trimer:



Monomer:



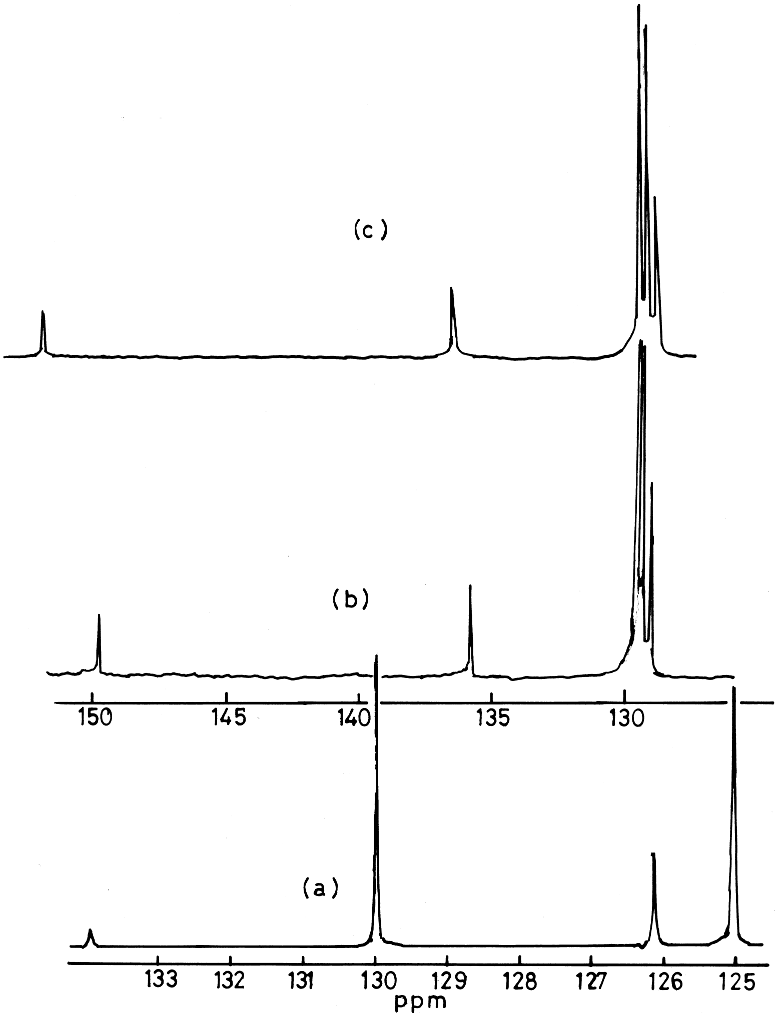


Figure 4. ^{13}C-NMR spectrum of (a) monomer, (b) trimer, and (c) polymer obtained by solution polymerization.

Table 3. ^{13}C-NMR of Phenylisocyanate Monomer, Polymer, and Trimer

	Monomer			
Assignment	δ_{calc}/ppm	δ_{obs}/ppm	Polymer δ/ppm	Trimer δ/ppm
C (1)	134.2	133.9	136.6	135.8
C (2)	124.9	125.1	129.9	129.0
C (3)	129.7	129.9	129.3	129.3
C (4)	125.7	126.1	129.0	129.4
C (5)	129.5	129.9	152.0	149.7

Therefore, the chemical shifts of C(1) and C(5) atoms attached to the N-atom of the trimer are larger than that of the monomer. The positions of carbons in trimer are more down field compared to that of the monomer. The largest change is observed for C(5), which has a chemical shift of 129.9 ppm in monomer and 149.7 ppm in trimer. In our previous work [21], for n-butylisocyanate the chemical shift of C(5) observed for monomer, trimer and, polymer were 125.0 (broad), 148.6, and 156.6 ppm, respectively. When the polymer was fractionated into different fractions, there were no noticeable differences in NMR spectra of these fractions.

Thermal Characterizations of Phenylisocyanate Polymer and Trimer

The products obtained by bulk and solution polymerizations of phenylisocyanate were studied by DSC and TGA to obtain thermal properties and information about the nature of products. The DSC thermograms for bulk polymerized samples at –20ºC are given in Figure 5. There are differences in thermograms of polymers obtained at different polymerization time. The samples obtained by 0.5 hours (Figure 5a) and 1 hour (Figure 5b) polymerization time shows small melting or/and T_g peaks, then intense exothermic peaks at about 162ºC that correspond with further polymerization given mostly mixed cyclic and linear products. At further polymerization time, the exothermic peaks are not observed, but the product still goes into changes with polymerization time given broad endothermic peaks. The glass transition temperature, T_g, (Figure 5d) is about 156ºC, which is expected to be high because of the rigid structure of the polymer chain. It can be observed much more easily for a polymer sample obtained after a 6 hour polymerization period (Figure 5d).

The TGA thermograms of bulk polymerized samples shows a similar pattern with some differences in peak positions and shape. The TGA thermogram of a sample obtained by a 3 hour polymerization time at –20ºC is given in Figure 6. The decomposition process takes place in three stages. About 13–15% decomposes at about 169ºC, 53–56% at about 219ºC and the rest at about 314ºC. Since the linear polymer is rodlike and stiff, it is expected to depolymerize upon decomposition. The thermal degradation products are also linear polymer, cyclic polymer, trimer, crosslinking through cyclization, etc.

The DSC and TG thermograms of trimer are given in Figure 7. The DSC thermogram gives a sharp endothermic (melting) peak at 279ºC. The TG thermograms show an intense degradation peak at 372ºC. Since the compound is completely crystalline, the peaks are quite sharp. These values are much higher than the transition and decomposition temperatures observed in thermograms (Figures 5– 6) of bulk polymerized at – 20ºC products. Therefore, the products do not contain trimer.

The DSC thermogram of bulk polymerized samples at 0ºC are given in Figure 8. There are no exothermic peaks unlike that of bulk polymerization at

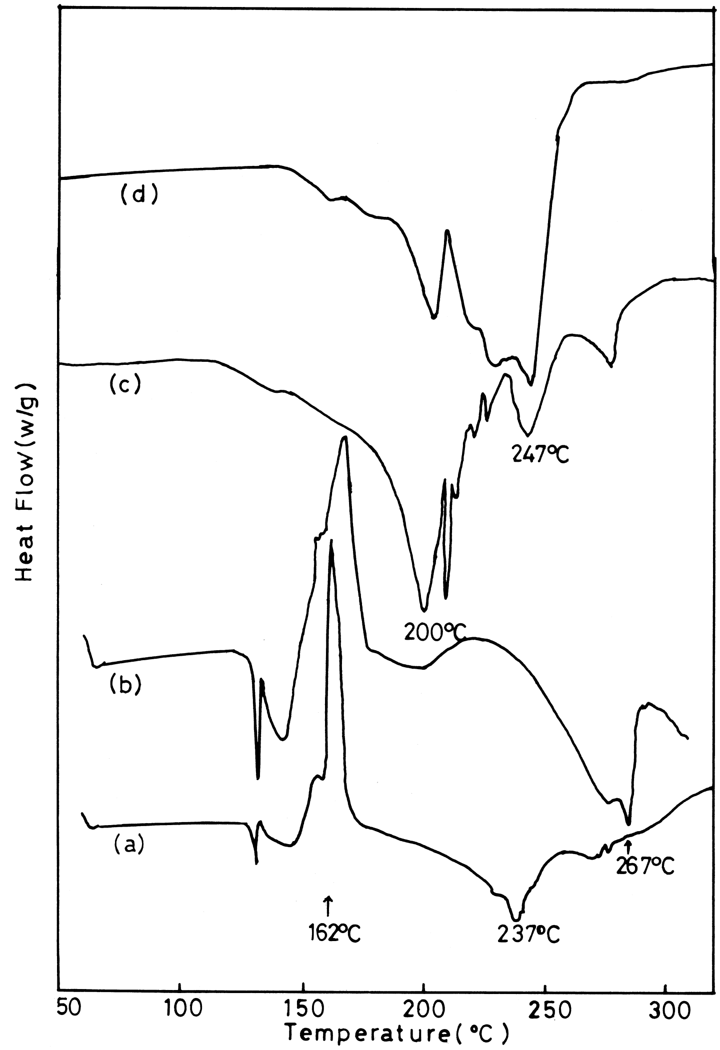


Figure 5. DSC thermograms of products obtained by bulk polymerization of phenylisocanate at –20°C and initiated with BC for (a) 0.5 hour, (b) 1 hour, (c) 3 hours, and (d) 6 hours.

– 20°C and melting shifts to higher temperatures with polymerization time. The number of endothermic peaks increased to three after 4 hours of polymerization time at 0°C (Figure 8c), and most probably also contain trimer. Since the peaks are broad, they may cover the glass transition. TGA thermograms gives decomposition in three stages, similar to polymerization at – 20°C with some differences in peak positions and intensities.

The DSC thermograms of samples obtained by solution polymerization at – 20°C are given in Figure 9. The thermogram of a 1 hour polymerization time (Figure 9a) shows one broad melting peak at 218°C and a sharp peak at 279°C.

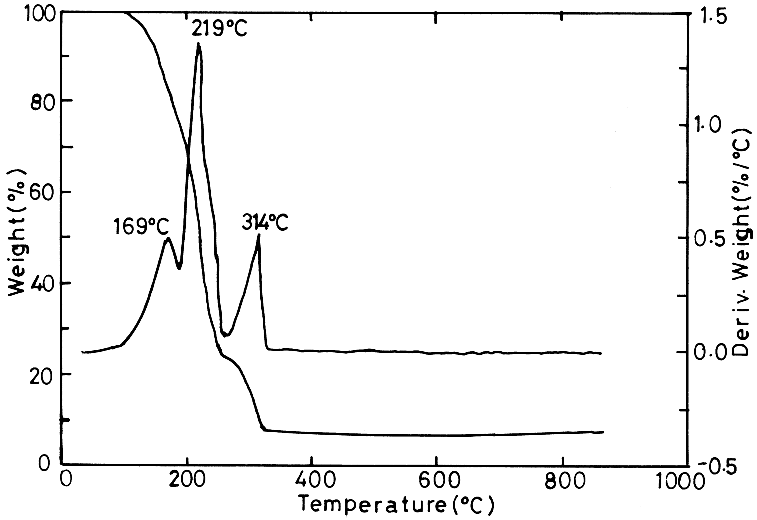


Figure 6. TGA of poly(isocyanate) obtained by CB at –20°C for 3 hours bulk polymerization.

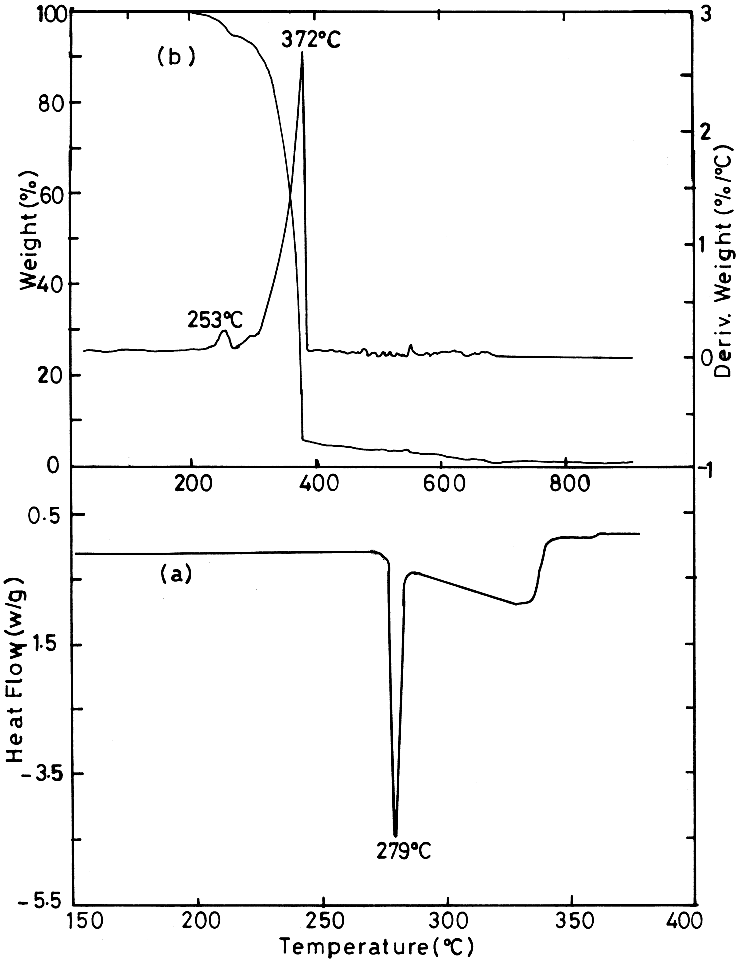


Figure 7. DSC and TGA thermograms of phenylisocyanate trimer.

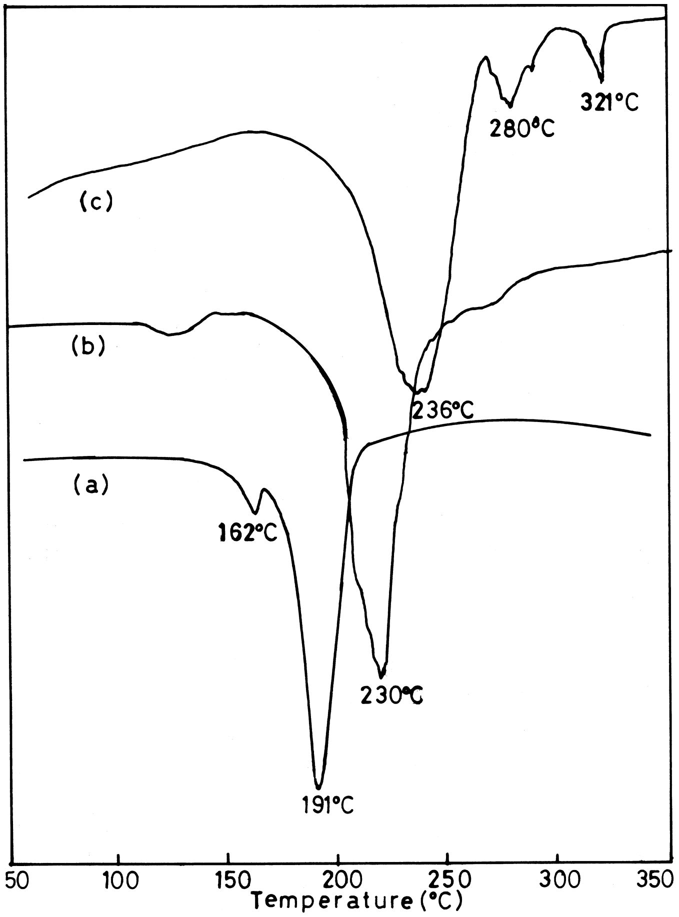


Figure 8. DSC thermograms of products obtained by bulk polymerization of phenylisocanate at 0°C and initiated with BC for (a) 0.5 hours, (b) 1 hour, (c) 4 hours.

The second peak is quite typical of a trimer, while the first one is that of a polymer. After a 2 hour polymerization, the peak at 218°C disappeared, but the trimer peak becomes more intense (Figure 9b). A broad peak at higher temperatures most probably indicates a cyclic polymer. This becomes more apparent after a 3 hour polymerization (Figure 9c). However, a new sharp peak at 185°C shows the rearrangement of a new product into a much more regular polymer structure. The thermal investigation of fractionated samples also clearly gives the presence of different linear and cyclic polymer, oligomers, trimer and dimer in the polymerization process. The process is quite dynamic and the polymer is a living type showing continuous changes before the living ends are eliminated. The TGA thermogram of the sample obtained by 3 hours' polymerization time is given in Figure 10. The decomposition is generally a depolymerization type and is quite similar to that of the trimer.

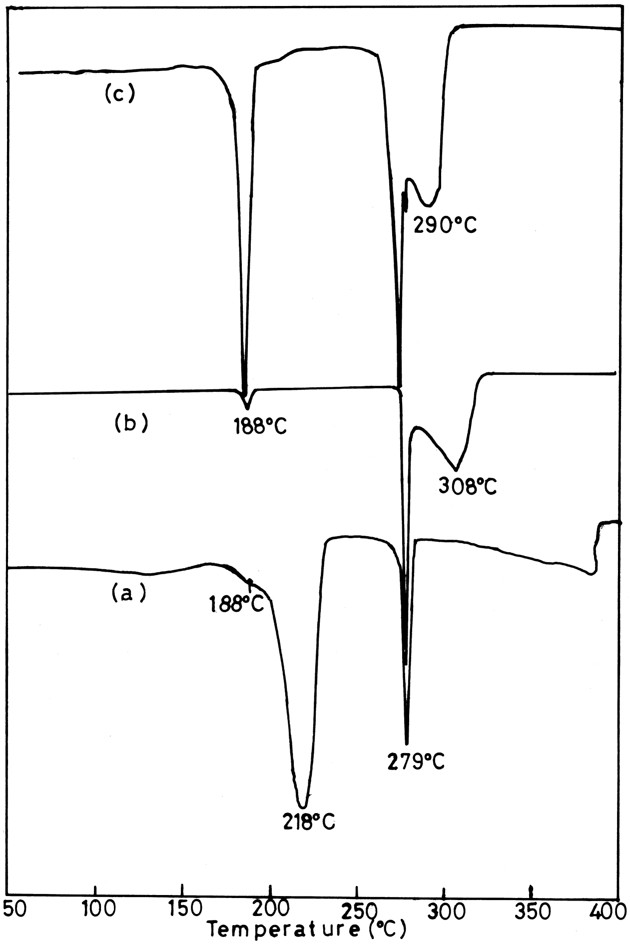


Figure 9. DSC thermograms of produ cts obtained by solution polymerization of phenylisocanate at –20°C and initiated with BC for (a) 1 hour, (b) 2 hours, and (c) 3 hours.

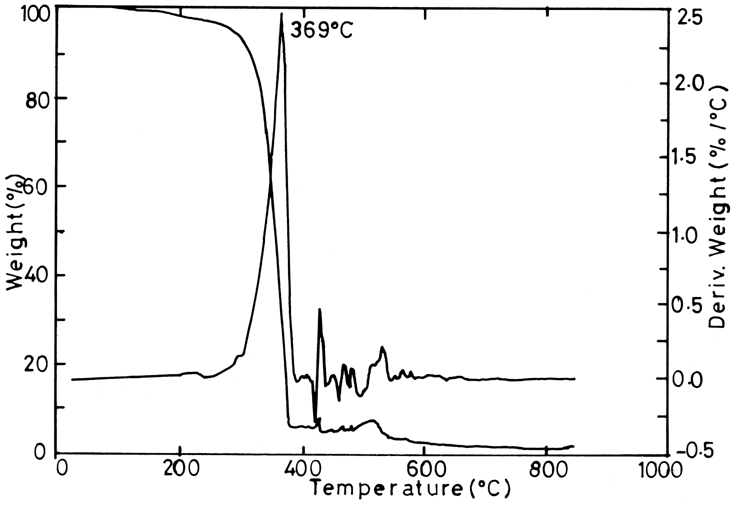


Figure 10. TGA thermogram of product obtained by solution polymerization of phenylisocanate at –20°C and initiated with BC for 3 hours.

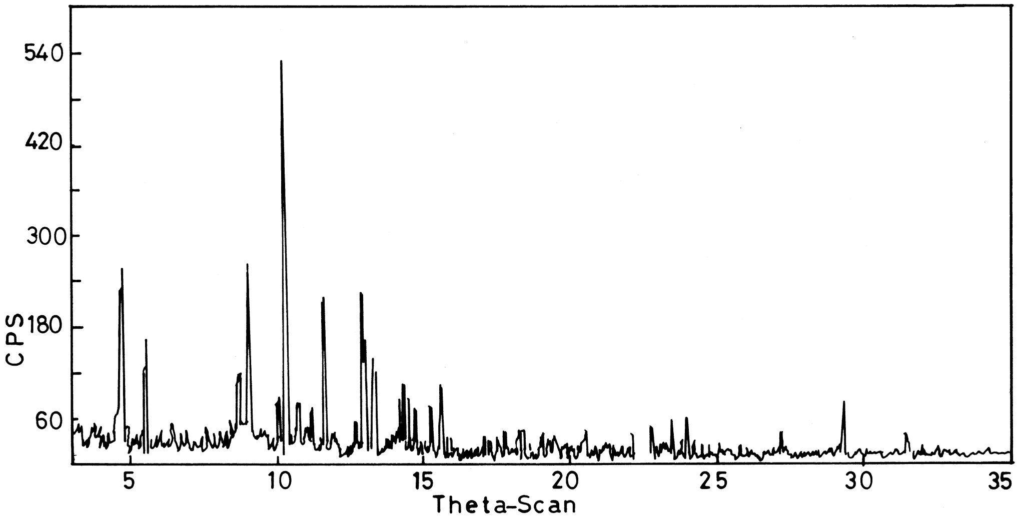


Figure 11. X-ray powder spectrum of acetic acid insoluble fraction of poly(phenylisocayanate).

X-Ray Characterization

The X-ray powder pattern of bulk polymreized samples showed the product to be partially crystalline. However, after fractionation, most of the products obtained were crystalline. As an example, the X-ray powdered spectrum of the insoluble fraction obtained after fractionation with acetic acid is given in Figure 11. The pattern was indexed for a monoclinic unit cell of a = 10.169, b=14.408, c= 16.908, and β = 99.91°. The space group was estimated as Pc. Most of the other fractions also gave a similar crystalline powdered pattern of very close cell parameters. The X-ray patterns of the polymer were different then that of the trimer, which was also taken in this work. As was shown previously [20], the most important evidence to differentiate between dimer, trimer, and polymer is the structural information obtained from the X-ray.

A more detailed work of the X-ray and mass spectroscopic characterization will be presented in another paper.

CONCLUSION

The results obtained can be summarized and concluded as follows:

The complex base (CB), $NaNH_2/(CH_3)_3CONa$, is an active catalyst in the polymerization of phenylisocyanate. When each base was used separately, $(CH_3)_3CONa$ gave a polymer, but $NaNH_2$ did not give a polymer. This is most probably due to the strength of $NaNH_2$ as a base. The depolymerization with a strong base predominates more than the polymerization reaction.

Phenylisocyanate polymerization by CB in solution has a slower rate than that in bulk. The main product in bulk polymerization is a high molecular weight polymer, but dimer, trimer and cyclic polymer were also formed in solution polymerization. This can be due to diffusion effects in the solution.

The polymer obtained was not completely soluble in any organic solvents tried. Therefore, the molecular weights were not measured.

According to the FT-IR spectral investigation, the polymers structure and other products obtained are almost the same. However, FT-IR results definitely proved the addition reaction was via C=N bond opening with the formation of a nylon-1 structure.

NMR spectral data gives small differences for different products, but the monomer has distinct differences. However, the crystalline polymer and trimer gives quite similar spectra.

The proposed mechanism will be presented in the next paper, after giving the details of the X-ray and Mass analysis.

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