The Effect of Alkyl Side Chain and Additives on the Anionic Polymerization of Isocyanates with Carbamate Group

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Summary: The synthesis of new isocyanate monomers and their polymerization by anionic route is reported. Reaction of 1,6-diisocyanatohexane with aliphatic alcohols such as methanol, n-propanol and n-pentanol in 1:0.5 molar ratios was carried out in the presence of pyridine such that one –NCO group remained unreacted. The anionic polymerization of n-alkoxycarbonylaminohexyl isocyanates was carried out using sodium napthalenide (Na-Naph) initiator in the presence of 15-crown-5 (15C5) and sodium tetraphenylborate as the additives. While polymerization of n-propyloxycarbonylaminohexyl isocyanate (PAHI) and n-pentanoxycarbonylaminohexyl isocyanate (PEAHI) was feasible that of methoxycarbonylaminohexyl isocyanate (MAHI) led to an insoluble material. The polymers were isolated in high yields with $NaBPh_4$ as the additive.

Keywords: additives; anionic polymerization; functional polyisocyanates; polyisocyanates

Introduction

Polyisocyanates have been studied extensively due to their helical structure and applications in various fields, such as materials for chiral recognition, optical switches, liquid crystals and degradable materials.[1–4] A number of functional poly(alkyl isocyanates)[5–12] and poly(aryl isocyanates)[13] have been synthesized to introduce chiral units in the side chain. Fuctionalized polyisocyanates with ether, ester and ketone groups[6] in the side chain form miscible blends with hydrogen bonding donor random coil polymers. Polyisocyanates with functional groups bearing active hydrogen, such as –OH, $–NH_2$, –COOH could strongly influence the helical structure of the polymer chain through polar interactions, and also useful in appending a variety of molecules through the side chain. However, direct synthesis of functional polyisocyanates bearing an active hydrogen in the side chain without proper protective groups is not feasible because of efficient proton abstraction and chain transfer reactions.

Okamoto and co-workers first reported the anionic polymerization of isocyanates with an active hydrogen in the side chain bearing a carbamate group (–NHCOOR, R = achiral or chiral alkyl group)[8] by using various achiral and chiral initiators in tetrahydrofuran (THF) at −98 °C and obtained polymers mainly having the 1-nylon structure. The polymerization of chiral monomers with achiral initiators gave the optical active polymers, and chirality situated at ten or eight σ-bonds from the polymer main chains affected the helical sense of the polymer. However, high molecular weight oligomers obtained from polymerization of the achiral monomer n-butoxycarbonylaminohexyl isocyanates by chiral initiators showed no optical activity. This was ascribed to intramolecular transfer of the propagation end to the carbamate group in the side chain in the initial stage of the polymerization. Clearly the chiral or

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achiral nature of the appended alkyl group on the carbamate moiety plays a vital role in preventing chain transfer.

Lee and co-workers polymerized similar isocyanate monomers with a bulky molecule N-Ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (Disperse Red1 or DR1) [10,11] and a chiral alkyl group[12] in the side chain using sodium napthalenide as the initiator in presence of 15C5 and $NaBPh_4$ as additives in THF at −98 °C. The resulting polymers were isolated in high yields exceeding 90% with narrow MWD under optimum conditions. Presumably the bulky DR1 or a chiral group on the side chain in the presence of the additives could effectively prevent chain transfer.

Here in we report the efficiency of the additives in preventing chain transfer in the polymerization of isocyanate monomers bearing small achiral alkyl groups. The living anionic polymerization of three monomers, methoxycarbonylaminohexyl isocyanate (MAHI), n-propyloxycarbonylaminohexyl isocyanate (PAHI) and n-pentanoxycarbonylaminohexyl isocyanate (PEAHI), in the presence of 15C5 and $NaBPh_4$ as additives is reported.

Experimental

Materials

15-Crown-5, methanol, n-propanaol, and n-pentanol (Aldrich) were used as received. 1,6-Diisocyanatohexane (98%, Aldrich) was stirred with CaH_2 overnight and distilled under reduced pressure. Tetrahydrofuran (Fisher, GR grade) was stirred with sodium overnight under reflux and distilled. Freshly distilled THF was stirred with Na-Naph solution in THF under high vacuum conditions with repetition of degassing procedures, and was distilled again prior to use.

Initiator

Na-Naph in THF was prepared from the reaction of small excess of naphthalenide with sodium at room temperature for 24 h. The reaction solution turned green, and it was frozen by liquid nitrogen to remove dissolved gas by connecting to high vacuum line (10^{-6} torr). After complete degassing of the solution, the initiator obtained from this solution was stored in a glass ampule with break seal under high vacuum at −30 °C.

Synthesis of the Monomers

MAHI, methoxycarbonylaminohexyl isocyanate, was prepared from the reaction between 1,6-diisocyanatohexane and methanol. To a mixture of 1,6-diisocyanatohexane (105.0 g, 625.0 mmol) and pyridine (2 ml), a solution of methanol (10.0 g, 312.5 mmol) in *n*-hexane (20 ml) was added drop by drop with stirring at 60 °C under nitrogen atmosphere. The reaction was stirred under reflux for 7 h. The solvent was removed from the mixture under reduced pressure at room temperature. The residue was distilled twice under reduced pressure (110 °C, 1 mmHg) and the distillate is the pure MAHI. Yield: 60%. ^1H NMR ($CDCl_3$) (ppm): δ 1.30–1.46 (m, 4H, $-(CH_2)_2-$), 1.47–1.56 (m, 2H, $-CH_2-$), 1.59–1.65 (m, 2H, $-CH_2-$), 3.13–3.18 (q, 2H, $-CH_2-NH-$), 3.20–3.34 (t, 2H, $-CH_2-$ NCO), 3.65–3.75 (s, 3H, CH_3-O-), 4.80 (s, 1H, –NH–), FT-IR (neat, cm^{-1}) : 1525 (N–H), 1702 (C=O), 2273 (N=C=O).

PAHI, n-propyloxycarbonylaminohexyl isocyanate, was prepared from the reaction between 1,6-diisocyanatohexane and propanol. To a mixture of 1,6-diisocyanatohexane (168.0 g, 1000 mmol) and pyridine (2 ml), a solution of propanol (30.0 g, 500 mmol) in *n*-hexane (20 ml) was added drop by drop with stirring at 70 °C under nitrogen atmosphere. The reaction was stirred under reflux for 7 h. The solvent was removed from the mixture under reduced pressure at room temperature. The residue was distilled twice under reduced pressure (120 °C, 1 mmHg) and the distillate is the pure PAHI. Yield: 56%. ^1H NMR ($CDCl_3$) (ppm): δ 0.93–0.95 (t, 3H, CH_3-), 1.30–1.46 (m, 6H, $-(CH_2)_2-$, $CH_3-CH_2-CH_2-$), 1.47–1.56 (m, 2H, $-CH_2-$), 1.59–1.68 (m, 2H, $-CH_2-$), 3.13–3.18 (q, 2H, $-CH_2-NH-$), 3.20–3.34 (t, 2H, $-CH_2-NCO$), 3.98–4.02 (t, 3H, CH_3-O-), 4.73 (s, 1H, –NH–), FT-IR (neat, cm^{-1}) : 1523 (N–H), 1701 (C=O), 2273 (N=C=O).

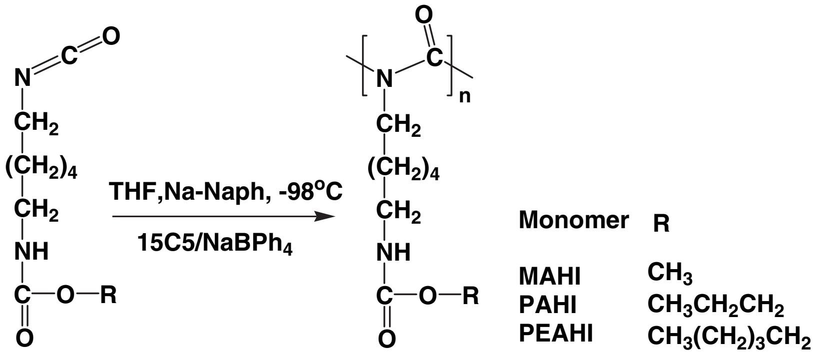
PEAHI, n-pentanoxycarbonylaminohexyl isocyanate, was prepared from the reaction between 1,6-diisocyanatohexane and pentanol. To a mixture of 1,6-diisocyanatohexane (67.2 g, 400 mmol) and pyridine (2 ml), a solution of pentanol (15.0 g, 170.4 mmol) in *n*-hexane (20 ml) was added drop by drop with stirring at 70 °C under nitrogen atmosphere. The reaction was stirred under reflux for 7 h. The solvent was removed from the mixture under reduced pressure at room temperature. The residue was distilled twice under reduced pressure (138 °C, 1 mmHg) and the distillate is the pure PEAHI. Yield: 52%. ^1H NMR ($CDCl_3$) (ppm): δ 0.88–0.92 (t, 3H, CH_3–), 1.30–1.46 (m, 6H, –$(CH_2)_2$–, CH_3–CH_2–CH_2–), 1.47–1.56 (m, 2H, –CH_2–), 1.59–1.68 (m, 2H, –CH_2–), 3.13–3.31 (q, 2H, –CH_2–NH–), 3.20–3.34 (t, 2H, –CH_2–NCO), 4.01–4.06 (t, 3H, CH_3–O–), 4.73 (s, 1H, –NH–), FT-IR (neat, cm^{-1}) : 1520 (N–H), 1701 (C=O), 2276 (N=C=O).

Anionic Polymerization of the Monomers

Anionic polymerization of the monomers was carried out in a glass apparatus equipped with break seals under high vacuum (10^{-6} torr), as a function of time at −98 °C (Scheme 1). The reactors were always pre-washed with the initiator solutions after being sealed off from a vacuum line. The initiator was introduced to the reactor, and cooled to −98 °C in a frozen methanol bath. Polymerization was initiated by adding monomer to the initiator solution. The reaction was terminated with the addition of acidified methanol to the reaction solution. The mixture was then poured into a large amount of methanol, and the precipitated polymer was filtered and dried under reduced pressure. To check the weight of unreacted monomers or trimers, the methanol soluble part was concentrated by evaporating it under reduced pressure and dried in *vacuo*.

Measurements

^1H NMR spectra were run using a JEOL JNM-LA300WB in $CDCl_3$ and the chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm. IR spectra were obtained using KBr pellets by the Perkin Elmer System 2000. Molecular weights of the polymers were calculated from the response of a multi-angle laser light scattering detector (Wyatt Technology) connected to a size exclusion chromatograph (MALLS/SEC). THF was used as the mobile phase at a flow rate of 1.0 mL/min. The dn/dc value for polymers in THF at 35 °C was measured with an LED (Optilab DSP) source. After dn/dc was measured for 5 different concentrations for one polymer sample, the average dn/dc



Scheme 1.
Polymerization of isocyanate monomers with carbamate side chains.

value 0.090 was used to gain SEC-LS data with refractive index detection at 35 °C.

Results and Discussion

Polymerization of the Isocyanates as Function of Time

Anionic polymerization of the monomers was performed using Na-Naph in THF at −98 °C varying the reaction time (Table 1) in the absence of the additives. Poly (methoxycarbonylaminohexyl isocyanate) (PMAHI) was insoluble in THF. The small methoxy group on the carbamate moiety presumably failed to prevent chain transfer from the main chain to the side chain. In the absence of the additives it is quite likely that intramolecular[8] and intermolecular chain transfer reactions occured leading to cross-linking.

Interestingly the other two monomers afforded polymers readily soluble in THF. Poly(n-propyloxycarbonylaminohexyl isocyanate) (PPAHI) took longer time to dissolve in THF than poly(n-pentoxycarbonylaminohexyl isocyanate) (PPEHAI). This indicated that increased side chain length led to decreased or complete prevention of cross-linking. For these two soluble polymers, however, the formation of trimer was observed within 10 min. reaction time. This is attributed to rapid initiation and propagation rates facilitating backbiting. Consequently the yield of the polymers decreased with time and hence it was difficult to control the polymerization unless an additive is used.

Polymerization of the Isocyanates with 15C5 as the Additive

Anionic polymerization of the three monomers was performed in the presence of 15C5 in THF at −98 °C (Table 2). 15C5 is known to effectively prevent backbiting in the living polymerization of certain isocyanate monomers[14] though it is not quite effective in the polymerization of simple monomers like n-hexyl isocyante (HIC). Polymerization of MAHI in the presence of additives led to the insoluble product, indicating that chain-end protection by the additive does not prevent chain transfer. For the other two monomers, soluble polymers were obtained as seen without the use of the additives. However, the polymerizations could be carried out for longer time with a steady increase in the yield. For PPAHI the yield was 88% at 30 min. That for PPEAHI was 87% and the reaction could be carried out until 50 min. Thus the cooperative effects of the additive and the steric bulk of the alkyl chain on the carbamate moiety minimize or prevent chain transfer to the pentant carbamate moiety. Nevertheless, the MWDs are quite broad and significant quantities of the trimers are formed indicating that 15C5 is not a very effective as an additive. For a better control over the MWD we used $NaBPh_4$ in place of 15C5.

Table 1.
Anionic polymerization of the isocyanates with carbamate group in THF at −98 °C.

Monomer	Na-Naph	Monomer	Time	$M_n \times 10^{-3}$		MWD M_w/M_n	Polymer Yield (%)
	mmol	mmol	min	calcd	obsd[a]		
MAHI	0.105	6.70	10	21.4	—	—	84 (16)[b]
	0.097	7.29	20	21.0	—	—	70 (30)[b]
	0.102	7.90	30	19.2	—	—	62 (38)[b]
PAHI	0.175	5.30	10	12.0	33.2	1.79	87 (13)[b]
	0.178	5.45	20	11.1	27.6	1.85	80 (20)[b]
	0.172	5.70	30	10.9	34.3	1.93	72 (28)[b]
PEAHI	0.186	5.21	10	11.9	20.1	1.67	83 (17)[b]
	0.196	5.43	20	11.1	22.3	1.70	78 (22)[b]
	0.188	5.15	30	10.5	18.6	1.75	75 (25)[b]

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 35 °C.

[b] The yields of the trimer are presented in parentheses.

Table 2.
Anionic polymerization of isocyanates with carbamate group in the presence of 15C5 in THF at −98 °C.

Monomer	Na-Naph	15C5	Monomer	Time	$M_n \times 10^{-3}$		MWD M_w/M_n	Polymer Yield (%)
	mmol	mmol	mmol	min.	calcd	obsd^a		
MAHI	0.162	1.62	7.65	10	11.1	–	–	70 (13^b/14^c)
	0.142	1.42	6.38	20	11.5	–	–	76 (24)^c
	0.152	1.52	6.80	30	6.8	–	–	45 (54)^c
PAHI	0.176	1.76	4.92	10	4.0	12.3	1.75	34 (63)^b
	0.183	1.83	5.18	20	7.3	34.2	1.69	61 (32)^b
	0.186	1.85	5.37	30	8.4	46.7	1.61	88 (10)^c
	0.235	2.30	4.19	50	8.3	63.4	1.88	78 (22)^c
	0.198	1.98	5.95	60	8.4	65.2	1.75	76 (24)^c
PEAHI	0.208	2.02	5.58	10	4.4	12.5	1.74	39 (58)^b
	0.197	1.98	5.59	20	7.3	12.9	1.77	50 (46)^b
	0.202	1.96	5.45	30	6.6	14.7	2.06	59 (35)^b
	0.213	2.10	5.78	40	10.0	18.9	2.04	72 (15^b/12^c)
	0.189	1.92	5.23	50	12.3	17.8	2.23	87 (11)^c

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 35 °C.
[b] The unreacted monomers are presented in parentheses.
[c] The yields of the trimer are presented in parentheses.

Polymerization of the Isocyanates with $NaBPh_4$ as the Additive

Table 3 shows the results of anionic polymerization of the monomers in the presence of $NaBPh_4$. In the polymerization of MAHI, once again, the major part of the product was the insoluble polymer. The methanol soluble part was the unreacted monomer and the trimer. The results were very similar as in the case of polymerization of the monomers with 15C5 as the additive. In the polymerization of the monomers in the presence of $NaBPh_4$, the decrease in yield of the polymer with time was slow, as against a rapid decrease in yield when 15C5 was used as the additive. After complete polymerization, $NaBPh_4$ functions as a more effective steric barrier than 15C5.[15–18] In case of polymerization of PAHI, at 40 min of the reaction time, highest yield was observed beyond which trimerization occurred. In the polymerization of PEAHI, the yield of the polymer was 95% even at 80 min of reaction time. These results indicate the effectiveness of $NaBPh_4$ in preventing backbiting as the length of side chain of the monomer increased. In other words, increased steric hindrance by the bulk

Table 3.
Anionic polymerization of isocyanates with carbamate group in the presence of $NaBPh_4$ in THF at −98 °C.

Monomer	Na-Naph	$NaBPh_4$	Monomer	Time	$M_n \times 10^{-3}$		MWD	Polymer Yield (%)
	mmol	mmol	mmol	min.	calcd	obsd^a	M_w/M_n	
MAHI	0.177	1.77	5.50	10	9.0	—	—	73 (19^b/8^c)
	0.181	1.81	5.71	20	8.9	—	—	86 (7^b/7^c)
	0.176	1.76	5.63	30	8.6	—	—	68 (32)^c
PAHI	0.160	1.60	5.23	10	11.2	19.9	1.37	76 (18^b/6^c)
	0.175	1.75	5.42	20	10.8	28.0	1.54	77 (14^b/9^c)
	0.190	1.90	6.07	30	11.6	29.7	1.56	81 (10^b/9^c)
	0.190	1.90	5.33	40	10.9	25.0	1.26	92 (8)^c
PEAHI	0.165	1.65	4.49	10	6.4	26.2	1.27	46 (54)^b
	0.197	1.97	4.65	30	8.0	30.5	1.25	67 (30^b/3^c)
	0.198	1.98	4.97	60	12.2	35.3	1.31	95 (1^b/4^c)
	0.175	1.75	5.60	80	15.0	42.0	1.36	92 (8)^c

[a] M_n and M_w/M_n were measured by SEC-LS in THF at 35 °C.
[b] The unreacted monomers are presented in parentheses.
[c] The yields of the trimer are presented in parentheses.

of the side chain alkyl groups augmented the additive power of $NaBPh_4$ resulting in very high yields with relatively narrow MWD.[8] However, compared to the MWD from true living anionic polymerization of monomers like HIC carried out in the presence of additives like $NaBPh_4$,[15] the MWD of PPAHI and PEAHI are not narrow. Also the calculated and experimental molecular weights greatly differ. Evidently, the polymerization of these isocyanate monomers is not straightforward.

The use of additives such as $NaBPh_4$ and bulky alkyl groups on the side chain considerably decrease chain transfer to the side chain, but probably do not entirely prevent it. In the process a certain part of the initiator gets used up, which could explain to some extent the discrepancy in the calculated and experimental molecular weights. The MWDs of the polymers obtained using $NaBPh_4$ as the additive clearly indicates that the cross-linking reaction is considerably minimized though not entirely prevented. A small degree of chain-transfer to the side chain becomes inconsequential since the amidate anion is weak, and in low concentrations cross-linking reactions become ineffective.

Recently we discovered that sodium benzanilide (Na-BA) is an excellent initiator in the polymerization of HIC as it does the dual function of initiation as well as chain-end protection.[19] We are currently using Na-BA and a number of related initiators to achieve greater control over the polymerization of carbamate isocyanates carrying different aliphatic and aromatic groups. Such control over polymerization would eventually allow easy access to the desired functional polyisocyanate by selective degradation of the carbamate moiety.

Conclusions

The effect of additives on prevention of backbiting and chain transfer in the polymerization of three aliphatic isocyanates obtained from the reaction of diisocyanates and aliphatic alcohols was investigated. The carbamate isocyanate bearing the small methyl group upon polymerization led to insoluble polymer, which was ascribed to cross-linking even in the presence of the additives. With increasing bulk of the side chain, soluble polymers were obtained, the yields of the polymers exceeding 90% even at long reaction time. Suppression of backbiting was more effective by the additive $NaBPh_4$ than 15C5. The control over the reaction increased with increasing bulk of the side chain alkyl group indicating that the steric bulk of the side chain and the additives cooperatively act in preventing trimerization as well as chain transfer.

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