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Isocyanate-Terminated Poly(ethylene Oxide)

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ABSTRACT

Isocyanate-terminated polyethylene oxide (PEO) was prepared by reaction of hydroxyl-terminated PEO of different molecular weights and toluene diisocyanate (TDI), at a molar ratio of 1:2. Reaction was carried out with and without catalyst (dibutyltin dilaurate). When catalyst was used, some chain extension accompanied the endcapping reaction. When endcapping reaction was carried out without catalyst, chain extension was minimal as determined from endgroup analysis and viscosity measurements. It was also found that secondary reactions of the terminal isocyanate groups led to further increase in solution viscosity after completion of the endcapping reaction.

INTRODUCTION

Poly(ethylene oxide) (PEO) is commercially available in a wide range of molecular weights. This polymer may be useful as a prepolymer either for the preparation of block polymers or for endcapping with reactive compounds containing a desired functional group. The major problem in carrying out such reactions successfully is the necessity of avoiding completely all side reactions and obtaining high,

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practically quantitative yields. If side reactions or low yields are encountered the modified PEO will be contaminated by side reactions products and by unreacted PEO. In most cases, purification and isolation of the desired product will involve rather tedious and time-consuming procedures.

The original hydroxyl or other more reactive terminal groups were used for such chemical modifications. Terminal hydroxyl groups as well as bromide and tosylate groups were used in endcapping of PEO with acid derivatives which have ultraviolet absorbing characteristics [1]. Aminated PEO was used for binding plant hormone carboxylic acid by salt formation [2, 3]. Terminal hydroxyl groups of PEO were converted to the corresponding sodium alcoholate derivatives and were used to initiate anionic block polymerization of some vinyl monomers, such as acrylonitrile [4] and methyl methacrylate [5].

Isocyanate-terminated prepolymers prepared by reactions between hydroxyl-terminated polymers and diisocyanate are widely used in the preparation of polyurethanes. Such prepolymers, of definite molecular weight, can be useful as starting materials for the preparation of block polymers or for endcapping with a desired functional group. These prepolymers are usually prepared by using a molar excess of the diisocyanate. When such a prepolymer is used, it is of practical interest that the prepolymer will be free of unreacted diisocyanate and that minimal chain extension will take place during endcapping reaction; thus the original molecular weight of the prepolymers will not be changed.

Among diisocyanates commonly used for this purpose, 2,4-toluene diisocyanate proved to be a satisfactory reactant [6]. Due to steric hindrance, the isocyanate group ortho to the methyl group is only about one tenth as reactive at 25°C as the isocyanate group para to the methyl. With increasing temperature the steric factor diminishes, until at 100°C both isocyanate groups have about equal reactivity [7].

It is expected that at room temperature reaction between terminal hydroxyl with isocyanate in the para position will be preferred over the reaction with isocyanate in the ortho position. Due to the difference in reactivity between these two groups, endcapping will dominate, and chain extension by reaction between isocyanate in ortho position with terminal hydroxyl will be minimized. It was already reported in the literature [8] that isocyanate-terminated urethane prepolymers were prepared by reaction of polyester glycol and 2,4-TDI by using molar ratio of reactants of 1:3. Upon completion of the capping reaction, the resulting prepolymer was quantitatively stripped of excess TDI by continuous extractions. The molecular structure of this prepolymer consisted of one molecule of the hydroxyl-terminated polyester which had been reacted on either ends with one molecule of TDI. When a molar ratio of 1:1.75 was used, polymerization also occurred.

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It would be of interest to ascertain whether PEO of different molecular weights can be converted into an isocyanate-terminated polymer by reaction with stoichiometric amount (1:2) of TDI with minimal chain extension of the PEO. Such prepolymers can be useful both for end-capping and block polymerization of PEO.

EXPERIMENTAL

Materials

PEO, TDI (80/20 mixture of 2,4 and 2,6 isomers), dibutyltin dilaurate (Fluka), and benzene (Frutarom) were used. Tetrahydrofuran (THF) (Frutarom) was dried by distillation from sodium benzophenone solution before use.

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Reaction between PEO and TDI

Reaction was carried out under dry argon in a closed flask equipped with a self-sealing rubber cap. Syringes were used for the introduction of reagents and removal of samples for analysis.

A typical procedure is described. PEO (3 g, MW 3000) was dissolved in benzene (50 ml) and was repeatedly dried by azeotropic distillation. The benzene was removed by vacuum distillation, and the PEO was dissolved in THF (50 ml). Dibutyltin dilaurate (0.05 ml) and TDI (0.28 ml) were added, and the reaction mixture was kept for 1 hr at 25°C under constant shaking.

Determination of Isocyanate Groups

Unreacted isocyanate groups were determined by titration with n-butylamine, by use of a known procedure [9]. The reaction between unreacted isocyanate and butylamine was completed by keeping the reaction mixture for 15 min at 80°C.

Determination of Unreacted TDI

Unreacted TDI was determined by GLC by using a Packard gas chromatograph, model 7300/7400. A glass column with solid support (Chromosorb W, 60-80 mesh) with 4% butanediol succinate as liquid phase at 130°C was used.

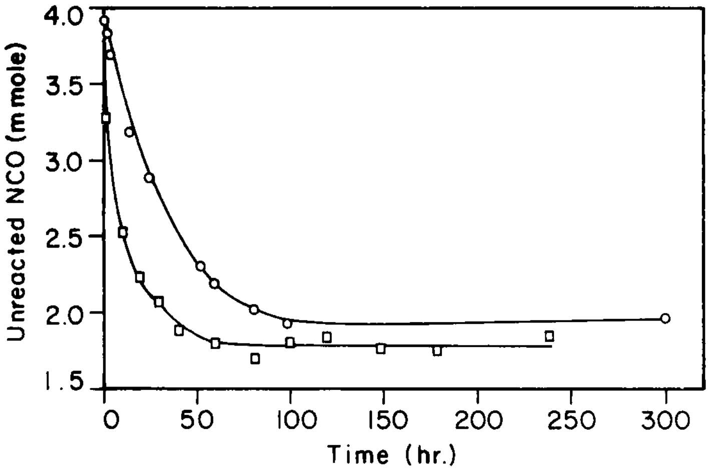

FIG. 1. Reaction between PEO and TDI: (○) reaction carried out without catalysis; (□) reaction carried out in the presence of dibutyltin dilaurate (0.05 ml). PEO (3 g, MW 3000) reacted in THF (50 ml) with TDI (0.28 ml) at 25°C, molar ratio of 1:2. Unreacted isocyanate groups were determined by titration.

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Viscosity Measurements

Viscosity measurements were carried out in a dry atmosphere by use of a Ubbelohde viscometer which was connected to calcium chloride drying towers.

RESULTS AND DISCUSSION

Endcapping of hydroxyl-terminated PEO of different molecular weights by reaction with TDI (80/20 mixture of 2,4 isomer and 2,6 isomer) in THF was investigated. A molar ratio of PEO to TDI of 1:2 was used. The reaction of PEO (MW 3000, $\overline{DP}_n$ = 68.2) with TDI was carried out with and without catalyst (Fig. 1). The catalyst used, dibutyltin dilaurate, maintains fair catalytic activity even in face of considerable steric hindrance at the isocyanate group [10]. The extent of TDI reaction was determined by titration of the unreacted isocyanate groups with butylamine. It can be seen that dibutyltin dilaurate catalyzes the reaction between TDI and hydroxyl-terminated PEO. By using a gas chromatographic (GC) technique it was found

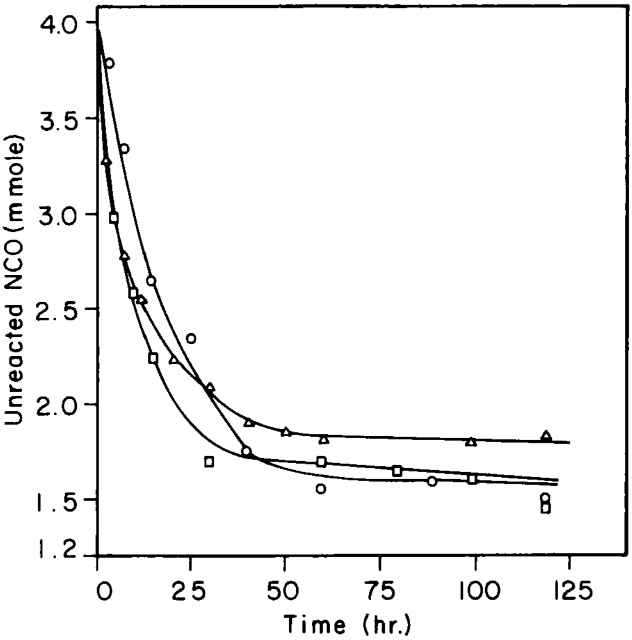

FIG. 2. Reaction between PEO of different molecular weight and TDI: (○) MW 1000; (△) MW 3000; (□) MW 6000. PEO (1.0 g, MW 1000; 3.0 g, MW 3000 6.0 g, MW 6000) reacted in THF (50 ml) with TDI (0.28 ml) in the presence of dibutyltin dilaurate (0.05 ml) at 25°C; molar ratio of 1:2. Unreacted isocyanate groups were determined by titration.

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that reaction with TDI was completed within 55 min. When catalyst was used, reaction was completed within 35 min. When reaction was carried out without catalyst, the $\overline{DP}_n$ of the endcapped PEO was not changed. The final value of free terminal isocyanate groups (1.95×10^{-4} mole) corresponds to $\overline{DP}_n$ of 69.9. Practically no polymerization could be detected by endgroup analysis. When reaction was carried out in the presence of dibutyltin dilaurate, the final value of free terminal isocyanate group corresponds to $\overline{DP}_n$ of 75.8. It seems that the catalyst decreased the selectivity of the reaction between the TDI and the hydroxyl-terminated polymer. More of the ortho isocyanate groups of the TDI reacted with free terminal hydroxyl groups, thus leading to polymerization. The 11% increase in $\overline{DP}_n$ of

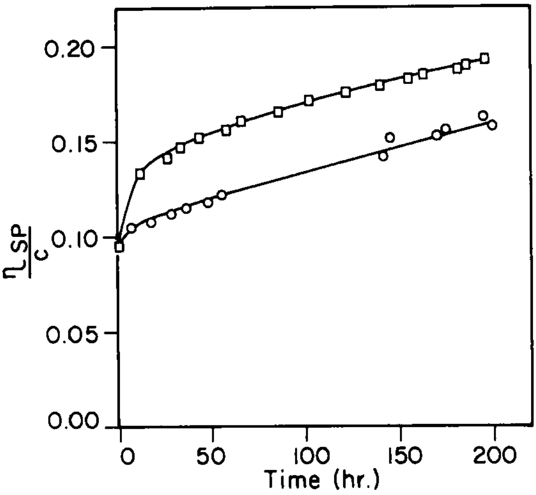

FIG. 3. Change in solution viscosity on reaction between PEO and TDI: (o) reaction carried out without catalyst; (□) reaction carried out in the presence of dibutyltin dilaurate (0.05 ml). PEO (3.0 g, MW 3000) reacted in THF (50 ml) with TDI (0.28 ml) at 25°C; molar ratio of 1:2.

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the endcapped PEO due to the introduction of urathane bonds along the PEO chain did not change its solubility in THF. Though some polymerization took place during the endcapping reaction, there is an advantage in using the catalyst if the isocyanate-terminated PEO is reacted later with another hydroxyl-containing molecule.

Reaction in the presence of catalyst was repeated with PEO of different molecular weights (Fig. 2). Similar results were obtained; endcapping was accompanied by some polymerization. When PEO of 1000 molecular weight was used $\overline{DP}_n$ of 28.8, corresponding to 27% increase in $\overline{DP}_n$, was found. When PEO of 6000 molecular weight was used, $\overline{DP}_n$ of 166, corresponding to 22% increase in $\overline{DP}_n$, was observed upon completion of the endcapping reaction.

Polymerization during the endcapping reaction can be easily detected by change in the viscosity of the reaction mixture. Reaction between the terminal isocyanate group and the terminal hydroxyl group will lead to a drastic change in molecular weight and will be detected by change in solution viscosity. Endcapping itself may change the viscosity of the polymer solution too, but not to the same extent as polymerization itself. From viscosity measurements (Fig. 3)

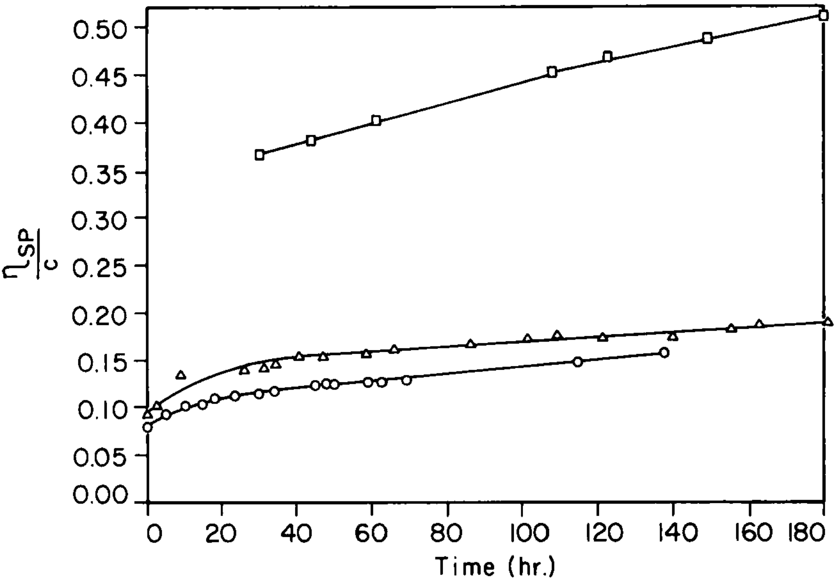

FIG. 4. Change in solution viscosity on reaction between PEO of different molecular weight and TDI: (○) MW 1000; (△) MW 3000; (□) MW 6000. PEO (1.0 g, MW 1000; 3.0 g, MW 3000; 6.0 g, MW 6000) reacted in THF (50 ml) with TDI (0.28 ml) in the presence of dibutyltin dilaurate (0.05 ml) at 25°C; molar ratio of 1:2.

it can be seen that under these reaction conditions, even before the completion of the endcapping reaction, some polymerization took place. Though no polymerization was observed by endgroup analysis when endcapping was carried out without catalyst, viscosity measurements indicated that some chain extension occurred. Nevertheless the extent of polymerization should be low, since it could not be detected by endgroup analysis. The presence of catalyst increases the extent of polymerization, as was found also by endgroup analysis. Similar results were obtained with PEO of different molecular weights (Fig. 4).

After the completion of the endcapping reaction, when the TDI is completely consumed, solution viscosity still increased to some extent (Figs. 3 and 4). This increase in viscosity can be attributed to secondary reactions of terminal isocyanate groups leading to drastic change increase in molecular weight. The extent of these reactions should be low, since no change in terminal isocyanate group concentration was found by endgroup analysis (Figs. 1 and 2). Such reactions

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can be the result of hydrolysis of terminal isocyanate groups or allophanate formation.

Allophanates formed by reaction between urethane groups of an endcapped PEO and terminal isocyanate group of another polymer will lead to chain extension and will be accompanied by an increase in solution viscosity. This reaction should lead eventually to crosslinking of the PEO. Since solubility of the endcapped PEO did not change with time and no change was observed in the final concentration of the isocyanate group, it may be assumed that allophanate formation under these reaction conditions should be negligible.

Most probably, the increase in viscosity is due to the presence of traces of water which could not be removed from the PEO by the drying procedure. Reaction between hydrolyzed terminal isocyanate groups and other terminal isocyanates will lead to chain extension which will increase the solution viscosity. In order to avoid these secondary chain extension reactions, the isocyanate-terminated PEO should be used immediately after completion of the endcapping reaction.

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