

Study on ternary polymerization of toluene diisocyanate

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Abstract: For the production of reactive polyurethane cross-linker and curing agents, 2, 4-diisocyanate toluene (TDI) terpolymer, which possesses the rigid structures of hexatomic ring and three reactive functional groups, was synthesized and characterized by the Fourier transform infrared (FTIR), the gel permeation chromatography (GPC) and the chemical analysis methods. The reaction conditions were studied and optimized. A tracking research on the polymerization process of TDI was taken by using the GPC. The formation processes of the terpolymer, oligomers and higher-polymers were also dealt with. Results show that the TDI terpolymer can be prepared in the presence of Cat-3 catalyst and at the reaction temperature of $(60 \pm 2)^\circ\text{C}$. The reaction time is short, its outcomes have narrow molecular weights distribution, namely molecular weights from 530 to 550, $M_w/M_n = 1.10$, and the mass fraction of NCO is $(25.0 \pm 0.5)\%$. With the reaction time prolonging, however, TDI can be further higher-polymerized to form higher-polymers. Benzoyl chloride (0.4%, mass fraction), as the stabilizing agent, can effectively inhibit the occurrence of higher-polymerization. The obtained TDI terpolymer can be stable for more than half a year.

Key words: 2,4-diisocyanate toluene; terpolymer; gel permeation chromatography; curing agent; storage stability

Under some reaction conditions, 2, 4-diisocyanate toluene (TDI) will undergo ternary polymerization to form the TDI terpolymer, which is also called isocyanurate. The molecules of isocyanurate possess the rigid structures of hexatomic ring, on which there is no active hydrogen atom. This property makes the products made from the TDI terpolymer have the outstanding practical performance in hardness, abrasion resistance, thermal stability, hydrolysis stability, solvent resistance and weather ability. Also, there are three reactive functional groups in the molecular structure of the TDI terpolymer, which makes it much more reactive than other kinds of isocyanates. The TDI terpolymer, therefore, is a good fast-speed curing agent. In recent years, it has been shown that it has wide applications in the fields such as elastomers, coatings, adhesives and foam plastics^[1-5].

The NCO group in the TDI molecule is strongly reactive; therefore, in addition to ternary polymerization, higher-polymerization will also take place in the progress of TDI polymerization, and this makes the resultant product become a mixture, affecting TDI's

practical performance adversely. The previous studies focused on speculating about the polymerization progress based on the changes in the viscosity of the reaction system, but this method lacked scientific evidence, and was hard to control accurately the molecular weight distribution of product. This paper conducts tracking research on the polymerization process of TDI by using the gel permeation chromatography (GPC), and deals with the formation process of the terpolymer and higher-polymers in the course of polymerization, and some factors which can affect the above process. Meanwhile, the resultant products are characterized by using the FTIR, and the storage stability of the TDI terpolymer is also studied.

1 Experimental

1.1 Raw materials and reagents

2, 4-toluene diisocyanate (Coronate T-100) industrial grade, NPU; Cat-3 analytical pure, manufactured by Shanghai Chemical Reagent Company; benzoyl chloride chemically pure, manufactured by Shanghai Chemical Reagent Company; di-n-butyl amine analytical pure, manufactured by Shanghai Chemical Reagent Company; ethyl acetate analytical pure, manufactured by Shanghai Chemical Reagent Company.

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1.2 Analytical instruments

PE series 200 GPC made by PE Company; FIR-750 Fourier transform infrared spectrometer made by Nicolet Company.

1.3 Synthesis of TDI terpolymer

Place 100 g of 2, 4-TDI monomer and 100 g of ethyl acetate into a dry 250 mL four-neck flask, which is equipped with the agitator, the thermometer and the reflux condenser. Flushed with N_2 as protection, the mixture is stirred at room temperature for 5 min, and then heated to 55 °C, and after that, the catalyst is added. The reaction mixture is heated to (60 ± 2) °C, and the reaction proceeds under the temperature. Aliquot (1 mL) was removed at various time intervals and examined the mass fraction of NCO group in the reaction system and for determining molecular weight and the molecular weight distribution by the use of the GPC. When the mass fraction of the NCO group drops to a proper value, the antipolymerizer benzoyl chloride is added to the mixture, and the mixture is continually stirred for 30 min so that the reaction goes on. Then, the final product is discharged. It is a viscous, pale yellow transparent product.

1.4 Analysis and test

1) Molecular weight measurement for the polymer

Polymeric molecular weight and its distribution is measured by using the GPC. Tetrahydrofuran is used as the solvent to dissolve the test sample, requiring the concentration of the solute (the test sample, namely the polymer) in the resulting solution is about 2%, so as to facilitate the measurement.

2) IR analysis

The test sample is dissolved in the THF (solvent) in the mass fraction of about 2%. The obtained solution is coated on the KBr pellet, and THF is totally evaporated under the irradiation of IR light; after completing the above steps, measure the resultant test sample.

3) Mass fraction analysis of the NCO group

This measurement is in compliance with GB 12009.4—89.

2 Results and Discussion

2.1 Principle of TDI terpolymerization

The presence of the NCO group in the TDI molecule enables TDI to have a tendency to polymerize, and it will undergo terpolymerization reaction to produce isocyanurate having the structures of hexatomic ring if any proper catalyst is present. The TDI

terpolymer's theoretical molecular weight is 522.6, and the mass fraction of NCO is 24.1%. The reaction formula is shown in Fig. 1.

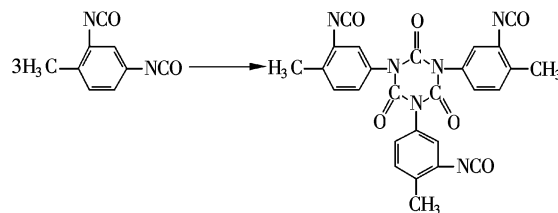


Fig. 1 TDI terpolymerization reaction

TDI terpolymerization is a nucleophilic reaction, in which trialkyl phosphine, tertiary amine and alkaline carboxylate can be used as catalysts^[6-7]. The terpolymerization reaction is irreversible. When it reaches a specific conversion rate, the constitute of the TDI monomers is very low, and the polymerization reaction will proceed between two or more polymerized oligomers until the spatial web-like arrangement of “long-chain” molecules forms. This arrangement makes the system become a gel. Products with various degrees of polymerization can be obtained by controlling different reaction conditions. Potential higher-polymers have structures as shown in Fig. 2.

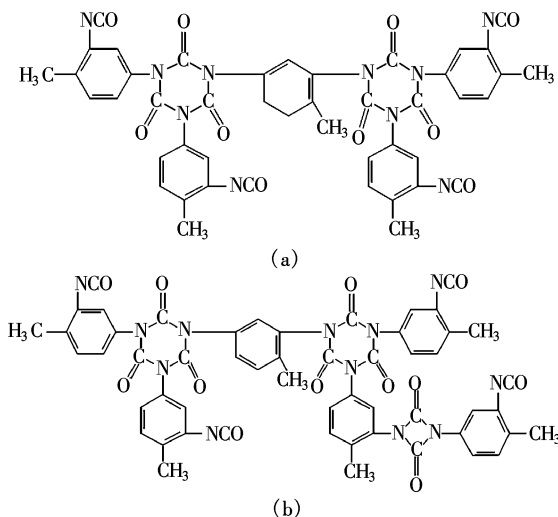


Fig. 2 TDI polymer. (a) Oligomer; (b) Higher-polymer

2.2 Effect of reaction time on mass fraction of NCO group

By adopting Cat-3 (Its mass fraction is 0.2% in the reaction system) as the catalyst, and keeping the reaction temperature at 65 °C, the sampling should be taken at the reaction time of 15, 30, 45, 60, 75, 90 and 105 min, respectively, and the mass fraction of NCO in the sample is measured respectively. The mass fraction of NCO vs. time is shown in Fig. 3.

From Fig. 3, it can be seen that after the reaction starts, the mass fraction of NCO in the system decrea-

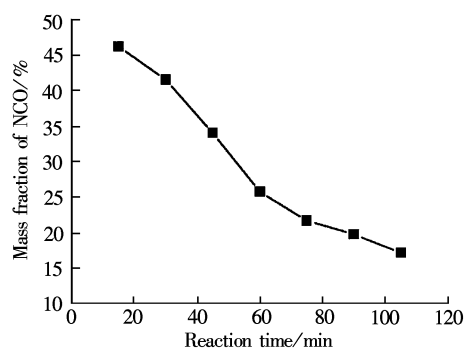


Fig. 3 Effect of the reaction time on mass fraction of NCO

ses sharply, and with the reaction time passing, the decrease tends to smoothness.

Theoretically, if all the TDI is polymerized to form terpolymer, $w(\text{NCO})$ should be 24.1%, namely half the starting value of $w(\text{NCO})$. If $w(\text{NCO})$ is smaller than 24.1%, it is suggested that there are higher-polymers formed in the product.

2.3 Effect of reaction temperature on TDI terpolymerization reaction

It is found that the polymerization reaction proceeded faster with the increase in reaction temperature. However, if the reaction temperature is too high, the product will become cloudy, viscous and deeper in color, and this will result in poor product performance. The effect of reaction temperature on reaction speed and product appearance is indicated in Tab. 1.

Tab. 1 Effect of the reaction temperature on reaction speed and product appearance

No.	Reaction temperature/°C	Time */min	Product appearance
1	40	118	Pale yellow, transparent
2	50	95	Pale yellow, transparent
3	60	60	Pale yellow, transparent
4	70	46	Brownish yellow, transparent
5	80	33	Brownish yellow, cloudy

Note: * The mass fraction of NCO is 24.5%.

2.4 IR spectral analysis of TDI terpolymer

The IR spectrograms of the TDI monomer and the TDI terpolymer are shown in Figs. 4 and 5, respectively.

In the IR spectrogram of the TDI terpolymer, the dissymmetry stretching vibrational absorption peak of the NCO group appears at the site of $2\,270\text{ cm}^{-1}$. There are three absorption peaks of the terpolymer at the sites of $1\,710$, $1\,410$ and 760 cm^{-1} , which show the appearance of the terpolymer in the product. There is an absorption peak of bipolymer at the site of $1\,600\text{ cm}^{-1}$, showing the presence of bipolymer in the product. There is no absorption peak at the site of $2\,130\text{ cm}^{-1}$, indicating no carbodiimide exists.

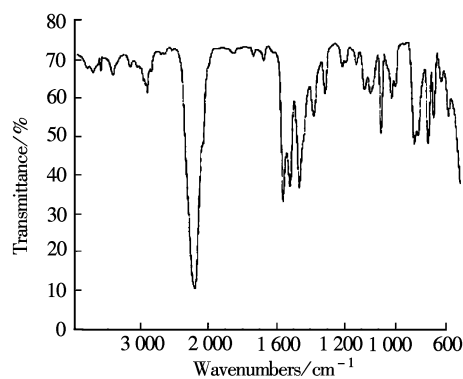


Fig. 4 IR of the TDI monomer

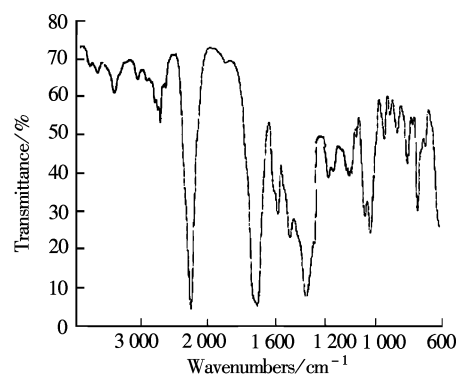


Fig. 5 IR of the TDI terpolymer

2.5 GPC analysis for TDI terpolymerization reaction process

During the course of self-polymerization reaction, the sampling is taken at the reaction time of 20, 40, 60, 80, 100 and 120 min, respectively, and the sample's molecular weight distribution is determined by using the GPC. The GPC spectrograms are shown in Fig. 6.

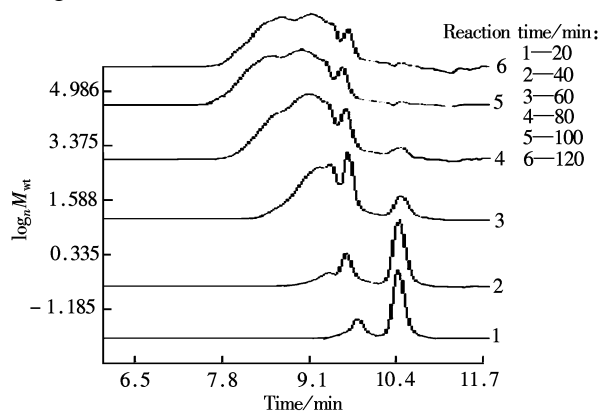


Fig. 6 GPC of the TDI terpolymer

In Fig. (6), the peak of reaction time at 10.43 to 10.41 min is the solvent peak; the peak of 9.80 to 9.70 min corresponds to the molecular weights from 530 to 550; the peak of 9.45 to 9.30 min corresponds to the molecular weight of 950; the peak of 9.15 to 9.08 min corresponds to the molecular weight of

1 050; the peak of 8.65 to 8.61 min corresponds to the molecular weight of 3 400.

It follows from the GPC spectrogram that, a single peak corresponding to the molecular weight of 530 or so appears at the reaction time of 20 min, showing the formation of the TDI terpolymer. The peak corresponding to the molecular weights from 530 to 550 becomes larger in size and a peak corresponding to the molecular weight of 950 or so is present at the reaction time of 40 min, showing the formation of TDI higher-polymers. At the reaction time of 40 min, the TDI monomer peak becomes smaller, and the peak corresponding to the molecular weight of 550 continues to enlarge in size. Also, the peak corresponding to the molecular weight of 950 becomes markedly larger. Meanwhile, a peak corresponding to the molecular weight of 1 050 or so appears. Based on the molecular weight, it is calculated that the formed products should be double the TDI terpolymer structural units and the bipolymer structural units consisting of double TDI terpolymer structures. At the reaction time of 80 min, the peak corresponding to the molecular weight of 550 becomes smaller, but the two peaks corresponding to the molecular weights of 950 and 1 055 continue to enlarge. At the reaction time of 100 min, the monomer peak almost disappears, and a peak corresponding to the molecular weight of 3 400 appears, showing the formation of the higher crosslinking degree of TDI higher-polymer structures. At the reaction time of 120 min, the peak corresponding to the molecular weight of 3 400 continues to become larger, but the acceleration of enlarging is not great.

This indicates that the reaction speed tends to become lower, when the mass fraction of the NCO group drops to a very low level. The above results are consistent with the described results in Fig. 3.

2.6 Storage stability of TDI terpolymer

The hexatomic ring of isocyanurate molecule in the TDI terpolymer possesses the strong electron-attracting effect, which causes the increase in electric potential difference of C—N bond within the NCO group, and so raises the reactivity. Therefore, in the course of TDI terpolymerization reaction, when the reaction reaches the desirable degree, the antipolymerizer must be added to deactivate the catalyst. If not added, the reaction will continually go further. In addition, when the TDI terpolymer is stored, three NCO groups in its molecular structure can react or be polymerized further with the moisture in the air, causing reduction in the mass fraction of the NCO group. So

the system becomes more viscous until entirely solidifying. Therefore, it is necessary to use the stabilizing agent to stop the reduction in the mass fraction of the NCO group.

This experiment uses benzoyl chloride as the stabilizing agent, and the mass fraction of its dosage is 0.4%. After the TDI terpolymer is treated in this way and kept in a sealed container for six months, there is little change in product performance. Even if you often open the container's cover to take the sample for use, the mass fraction of the NCO group in the sample only decreases by 28%, representing a better stable performance (see Fig. 7).

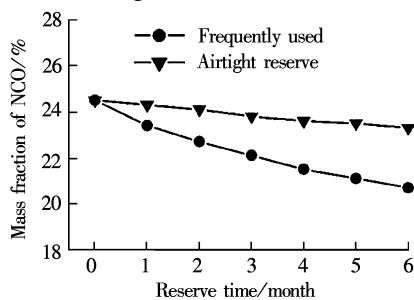


Fig. 7 Stability of TDI terpolymer

3 Conclusions

1) The TDI terpolymer products with better quality can be obtained by using Cat-3 as the catalyst, keeping the appropriate reaction temperature and reaction time.

2) When TDI self-polymerization reaction takes place, the TDI terpolymer is produced first, and then with the reaction proceeding, the TDI higher-polymers will be further produced. And with the reaction time prolonged, the resultant polymers will have larger molecular weights. At the reaction temperature of $(60 \pm 2)^\circ\text{C}$, to obtain the ideal terpolymer products, the preferable reaction time should be within 60 min. Its outcomes have narrow molecular weight distribution; namely, molecular weights range from 530 to 550, $M_w/M_n = 1.10$ and the mass fraction of NCO is $(25.0 \pm 0.5)\%$.

3) Using benzoyl chloride (its mass fraction is 0.4% in the reaction system) as the stabilizing agent, the obtained TDI terpolymer can be stored stably for more than half a year.

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甲苯二异氰酸酯三元聚合反应的研究

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摘要: 为了制备高活性聚氨酯交联固化剂, 用 2,4-二异氰酸基甲苯(TDI)三元聚合反应合成了具有 3 个活性异氰酸根的六元环结构异氰脲酸酯。用红外光谱、凝胶色谱(GPC)及化学分析法对反应条件进行了优化研究, 并对产物进行了表征。利用凝胶色谱法对 TDI 三聚体及多聚体的形成过程进行过程跟踪, 并对 TDI 三聚体的稳定性进行了研究。结果表明: 采用 Cat-3 作催化剂, 在 $(60 \pm 2)^\circ\text{C}$ 下反应, 可制得分子量为 530 ~ 550, $M_w/M_n = 1.10$, NCO 质量分数为 $(25.0 \pm 0.5)\%$ 窄分子量分布的 TDI 三聚体; 随着反应时间延长, TDI 会进一步多元聚合生成多聚结构; 而加入质量分数为 0.4% 的苯甲酰氯作为稳定剂, 可有效抑制多元聚合的发生, 所制备的 TDI 三聚体稳定性可在半年以上。

关键词: 2,4-甲苯二异氰酸酯; 三聚体; 凝胶色谱; 固化剂; 贮存稳定性

中图分类号: O63; TQ43; TQ31