Polymer Bulletin 45, 223–229 (2000)

Polymer Bulletin

Synthesis and properties of poly (1,4-cyclohexanedicarboxylic anhydride)

Tao Zhang[1], **Ming Gu**[2], **Xuehai Yu**[1*]

[1] Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering
[2] Laboratory of Solid State Microstructures, Nanjing University, Nanjing, Jiangsu 210093, People's Republic of China

Received: 24 May 2000/Revised version: 4 September 2000/Accepted: 6 September 2000

Summary

Polyanhydrides from cycloaliphatic 1,4-Cyclohexanedicarboxylic acid (1,4-CHDA) were synthesized by melt polycondensation and characterized by WAXD, FTIR and DSC. The results show that these polymer displayed strong crystallinity with highly melting point and can't be dissolved in common solvents. The polymers, which come from different original isomer conformation CHDA, show different melting point and DSC curve. The isomerization happened during the polymerization and reached an equilibrium point at last. By melt polycondensation, the high cis-isomer content polyanhydride is difficult to obtained.

Introduction

The first polyanhydride study is the synthesis of the poly(terephthalic anhydride) and poly(isophthalic anhydride) by Brucher and Slade (1) in 1909. In 1930's, Hill and Carothers (2, 3) prepared a series of aliphatic polyanhydride such as poly(adipic anhydride) and poly(sebacic anhydride) etc in attempting to be mold as chemical fibers. But due to the hydrolysis of anhydride bond, the fiber loses its strength and pliability rapidly. After that, Conix (4, 5) synthesized a series diacids of bis(*p*-Carboxyphenoxy), bis(*p*-Carboxyphenyl) and bis(*m*-Carboxyphenoxy) alkylene and the polyanhydride fibers with better properties than those based on aliphatic acid only were prepared. On the other hand, Yoda prepared a number of copolyanhydride by mixing terephthalic acid with adipic acid or sebacic acid, and then dehydrate by acetic anhydride. In addition, Yoda (6) also synthesized many of new polyanhydrides such as aromatic polyanhydrides, heterocyclic polyanhydrides, poly(amide anhydrides) and polyanhydrides containing thioether and sulfone linkage along the polymer main chain. These polyanhydride have suitable melting point, glass transition point, crystallinity and crystallization rate, the fiber and film forming properties as well as hydrolysis resistance got a great progress.

Unfortunately, as compared with the polyester, polyamide, polypropylene and polyacrylonitrile fiber etc., the hydrolysis resistance still can't satisfy with the requirement of the commercial product. So, the research of polyanhydride was almost stopped after 1960's. But just noticed the hydrolysis of polyanhydride, Langer et al. began to study the polyanhydride using in drug-controlled release in 1970's. Since then, polyanhydride has been intensively studied as matrices of drug controlled system for its

---

[*] Corresponding author

excellent biocompatibility and surface eroding (7-10). Similar with the general polymers, the properties of polyanhydride are greatly affected by the chemical structure of the backbone. In the previous studies, the aliphatic polyanhydride (11-14), the aromatic polyanhydride (15) and the aliphatic-aromatic polyanhydride (16) have been synthesized and studied. These studies showed that the aliphatic polyanhydrides degrade in a few hours while some aromatic polyanhydrides degrade over a few years (16). Hence many researchers are looking for new polyanhydride to satisfy the requirement of drug delivery system. In this paper, a new cycloaliphatic polyanhydride based on 1,4-cyclohexanedicarboxylic acids with different conformations were prepared and the structures and the isomerization during the polymerization were studied.

1,4-cyclohexanedicaboxylic acid, or be named as hexahydroterephethalic acid, and its diesters are important monomers in synthesis of polyester or polyamide. In the studies of polyesters and polyamide etc., the cis, trans conformation and the isomerization between the two isomers are particularly interest problem and have been conducted by many scholars (17-21), especially in liquid crystal polyesters (21). However, similar report has not been seen in the polyanhydride studies. One of our aims is to give some hints in this field.

Experimental

Materials and Instruments

1,4-Cyclohexanedicarboxylic acids were kindly provided by Dr. S. Liang of Eastman Chemical Company as high purity (the assay as total CHDA is 99.97%). All the solvents have been dried by 4A molecular sieve and distilled before used.

The cis isomer assay in the original CHDA is 74%. The CHDA of high cis-isomer content (cis-1, 4-CHDA) was obtained by refluxing the original CHDA (20g) in 200ml distilled water for 1 hour firstly, the obtained hot solutions was filtered and then concentrated to dry to get the cis-1,4-CHDA 14g, m.p.170-172°C. The high trans-conformation isomer content CHDA (trans-1, 4-CHDA) was obtained by converting cis-1, 4-CHDA as described below (21). In a Kimax tube, to which a slender tube had been inserted to the bottom, cis-1, 4-CHDA was filled. After replacing the atmosphere for 4 hours by conducting the dried nitrogen through the slender tube, the Kimax tube was immersed into a salt bath at 290-295°C and heated for 0.5 hour. During this time the sample melted first and then gradually resolidified. After cooling to room temperature, the sample was transferred to a flask and stirred under reflux with chloroform for 1 hour. The undissolved solid was collected by suction filtration and washed on the Buchner funnel with several small portions of $CHCl_3$, then sucked dry and recrystallized from anhydrous alcohol, m.p.310-313°C.

Thermal analysis were conducted with a Setaram DSC131 in aluminum pans at a heating rate of 10°C/min under nitrogen. IR spectra were measured with a Nicolet 170SX FT-IR spectrometer in KBr pellets. Wide-angle X-ray diffraction of the polymer in the form of pressed discs was recorded in a Rigaku D/Max-RA rotating anode X-ray diffractometer using a CuKα source. The polariscope photographs were taken on Wild MPS 51S on Leitz 350 polariscope with zoom out 320 times.

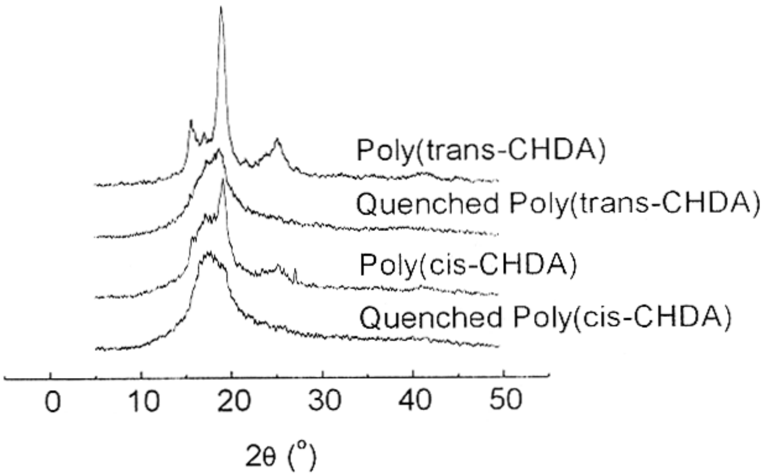
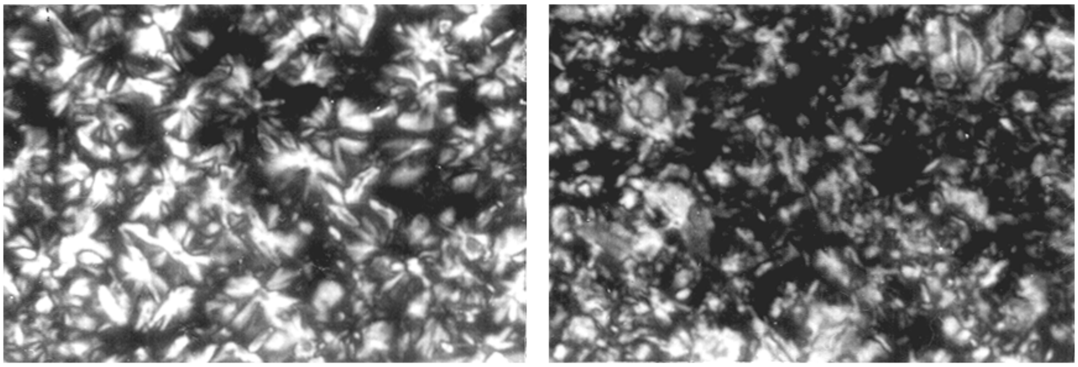


Figure 1. The XRD of poly(cis-CHDA) and poly(trans-CHDA)



Poly(cis-CHDA) Poly(trans-CHDA)

Figure 2. The polariscope photograph of the poly(cis-CHDA) and poly(trans-CHDA)

Thermal Analysis

Figure 3 shows the DSC curves of poly(trans-CHDA), poly(cis-CHDA) and poly(CHDA). The small endothermic peaks of the poly(trans-CHDA) at 120°C and 140 °C are assigned to the short-range structures. At about 250°C, the melting point peak is obviously. For the poly(CHDA), the endothermic peak at about 235°C gives melting point clearly. The same melting range was also been observed with a microscope in melting point tube. At about 280°C to 300°C, polymers show thermal decomposition. This result is as same as determined on TA Inst2100 thermo-gravimetric analyzer.

It is interested to note the poly(cis-CHDA) curve that the peak at about 130°C is also assigned to the short-range structures. But from 165°C to 220°C, the curve gives a series of small endotherms. We believe that this kind of continued endothermal is attributed to the process of isomerization of cis-isomer conformation to trans-isomer conformation and no clear melting point could be observed. To prove this assumption, an annealing sample of poly(cis-CHDA) at 165°C for 1hr which shows the same curve of poly(CHDA).

Polymerization

Poly(1,4-cyclohexanedicarboxylic anhydride) was synthesized by melt polycondensation (22) and the whole polymerization program can be seen as two periods: the synthesis of prepolymer and the polycondensation. CHDA anhydride prepolymer was prepared by refluxing the CHDA monomer (10g) in acetic anhydride (100ml) for 1 hour. The access acetic anhydride was removed to dry under vacuum at 100°C and the residue was dissolved in 20ml $CHCl_3$, then adding the solution to anhydrous ethyl ether with stirring to precipitate the prepolymer. The precipitation was then extracted in Soxhlet's extractor by ethyl ether for 24 hours to remove trace of the acetic anhydride.

The melt-polycondensation was carried out as follows: CHDA prepolymer was mixed with 2 molar percent Cadmium Acetate (catalyst) in a Kimax tube and after been vacuumized and filled with dried nitrogen for 3 times, the tube was immersed into a salt bath at 280°C. After the prepolymers were melted, high vacuum (<5Pa) was applied through the side arm for about 1.5 hours and the condensate (acetic anhydride) was collected in a liquid nitrogen trap. After the polymerization finished, $CHCl_3$ was used to extract the crude polymer in Soxhlet's extractor for 24h.

Poly(cis-1, 4-CHDA anhydride) and Poly(trans-1, 4-CHDA anhydride) were synthesized similarly as described before. But the polymerization temperature were kept in 170-180°C and 270-280°C respectively.

Results and discussion

Crystallization of polyanhydride

The polyanhydride of the high cis-isomer content CHDA (Poly(cis-CHDA)), the high trans-isomer content CHDA (Poly(trans-CHDA)) and the original CHDA (Poly(CHDA)) were synthesized by the melt polycondensation. No matter which isomer was used, the obtained polyanhydride is a kind of insoluble brittle polymer with high melting point. These properties are so similar to the poly(terephthalic anhydride) and poly(isophthalic anhydride) (1,23) and the determination of the molecular weight is difficult. It is inferred that these properties are attributed to the high crystallization of the polymer and the presumption was proved by the wide angle X-ray diffraction analysis. Figure 1 shows the XRD spectrum of poly(cis-CHDA), poly(trans-CHDA) and their quenched production from melting to liquid nitrogen. At about 20 and 25 degree, both the poly(cis-CHDA) and poly(trans-CHDA) show strong crystalline peaks, and another peak appears at 15 degree on poly(trans-CHDA). It was indicated that all the polymer shows high crystallization and the poly(trans-CHDA) exhibits much higher crystallinity than the poly(cis-CHDA). After been quenched from melting to liquid nitrogen, the crystal peak is remaining highly.

Figure 2 shows the polariscope photograph of the poly(cis-CHDA) and poly(trans-CHDA). They are taken after been heated to melt and then cooled to crystallize. The spherulite of poly(cis-CHDA) is smaller than which in the poly(trans-CHDA).

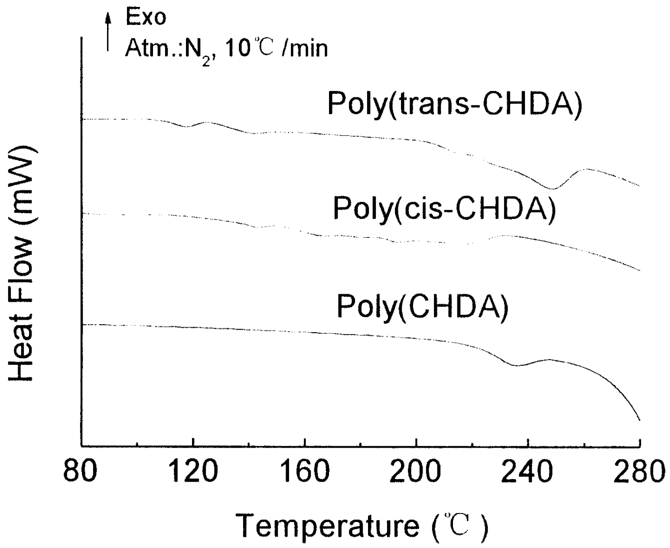


Fig 3. DSC of poly(CHDA), poly(trans-CHDA) and poly(cis-CHDA)

From the curves, the melting point of polymer containing cis-isomer conformation is lower than that of polymer containing trans-isomer conformation. This can be attributed to the lower crystallization and the smaller spherulite, which have been shown in XRD, Figure 1, and polariscope photograph, Figure 2.

Isomerization during polymerization

For the isomerization of the trans, cis-isomer conformation of 1,4-CHDA, there is a great difference between the properties of the cis- and trans-isomer conformations. For example, the melting point of the cis-CHDA monomer is 170-171 °C (24), but for the trans-CHDA, it is 312.5°C (25). Whether the isomerization exists and the influence of the isomerization to the properties of polyanhydride is an interesting problem. In the polycondensation of cis-CHDA at 170-180°C which is just above its melting point, the reaction system become solidification after 2 hours. But if the reaction system is heated to 250°C, then it returns to liquid state because of the melting of poly(cis-CHDA) and poly(trans-CHDA). These phenomena are attributed to the converting cis-conformation to trans-conformation. When the temperature reached 180 °C, the converting rate is accelerated and the solidification is observed quickly.

Figure 4 shows the FTIR spectrum of polyanhydride made from high trans-isomer content CHDA, high cis-isomer content CHDA and original CHDA. In fact, the FTIR spectrum of poly(cis-CHDA) is so similar to the poly(CHDA) that they can't be distinguished. However, on the spectrum of poly(trans-CHDA), the peaks at 1700.6, 1423, 1265.9 and 1202cm^{-1} wavenumber can't be found on the other two spectrums. Although the peaks have not been assigned exactly, the difference can only be explained as the conformation difference between the two isomers. It is deduced that the cis-isomer CHDA began to convert to the trans-isomer at the polymerization temperature(170°C) and finally reached to an equilibrium state. So the polymer is as same as the polyanhydride made from original CHDA. But for the trans-CHDA, the isomerization temperature is too high to give enough amount of cis-isomer at polymerization temperature, the polyanhydride kept its trans-isomer conformation of 1,4-CHDA.

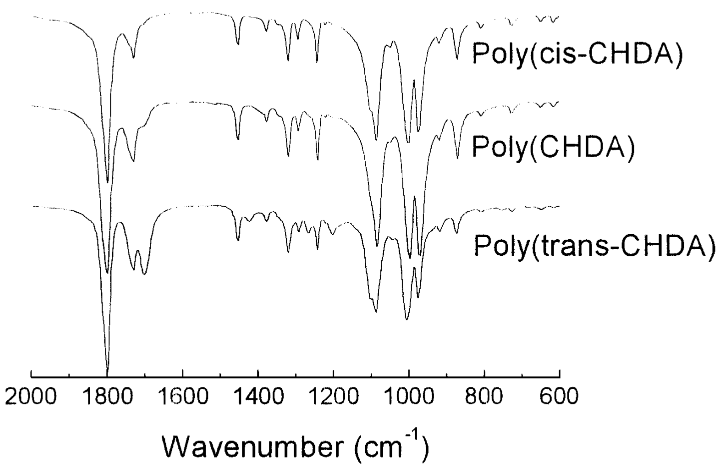


Fig 4. The FTIR spectrum of poly(cis-CHDA), poly(trans-CHDA) and poly(CHDA)

Figure 5 shows the FTIR spectrum of poly(cis-CHDA) polymerized at different temperature. In the spectrum, one of the poly(cis-CHDA) is polymerized below 180°C for more than 2 hours to solidification, the other one is polymerized below 180°C to solidification and then heated to 280°C to continue melting polymerization. From the spectrum, the poly(cis-CHDA) polymerized below 180°C is as same as the spectrum of poly(CHDA) which is just the represent of the equilibrium point at this temperature. But when heated to the higher temperature, the former equilibrium state is shift the cis-isomer CHDA to more-trans-isomer CHDA state during the temperature increasing until the most cis-isomer has been converted to trans-isomer conformation, so the spectrum is similar to that of the poly(trans-CHDA).

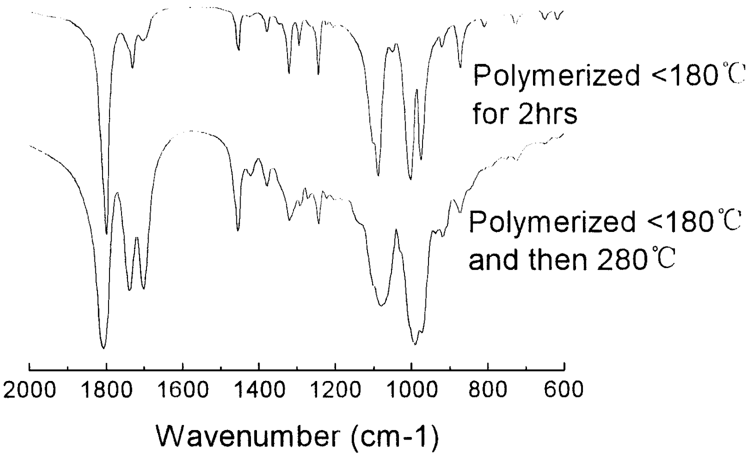


Fig 5. The FTIR spectrum of poly(cis-CHDA) polymerized at different temperature

References

1. Bucher JE, Slade WC (1909) *J. Am. Chem. Soc.* **31**: 1319.
2. Hill JW, Carothers WH (1932) *J. Am. Chem. Soc.* **54**: 1569.
3. Carothers WH, Hill JW (1932) *J. Am. Chem. Soc.* **54**: 1549.
4. Conix A (1957) *Makromol. Chem.* **24**: 76.
5. Conix A (1958) *J. Polym. Sci.* **29**: 343.
6. Yoda N (1969) Polyanhydride. In: Mark HF(ed) *Encyclopedia of Polym. Sci. Eng. Tech.* Vol. 10 John Willy & Sons, New York.
7. Rosen HB, Chang J, Wnek GE, Linhardt RJ, Langer R (1983) *Biomaterials* **4**: 131.
8. Leong KW, Brott BC, Langer R (1985) *J. Biomed. Mater Res.* **19**: 941.
9. Leong KW, Amore PD, Marletta M, Langer R (1986) *J. Biomed. Mater Res.* **20**: 51.
10. Leong KW, Kost J, Mathiowitz E, Langer R (1986) *Biomaterials* **7**: 364.
11. Albertsson AC, Lundmark S (1990) *Brit. Polym. J.* **23**: 205.
12. Ropson N, Dubois PH, Jerome R, Teyssie PH (1997) *J. Polym. Sci., Part A: Polym. Chem.* **35**: 183.
13. Domb AJ, Maniar M (1993) *J. Polym. Sci., Part A: Polym. Chem.* **31**: 1275.
14. Domb AJ, Nudelman R (1995) *J. Polym. Sci., Part A: Polym. Chem.* **33**: 717.
15. Domb AJ (1992) *Macromolecules* **25**: 12.
16. Domb AJ, Gallardi CF, Langer R (1989) *Macromolecules* **22**: 3200.
17. Kiefer LA, Yoon YH, Glass TE, McGrath JE (1992) *Polym. Prepr.* **33**: 227
18. Srinivasan R, Moy T, Saikumar J, McGrath JE (1992) *Polym. Prepr.* **33**: 225.
19. Tenkovtsev AV, Rutman AB, Bilibin AY (1992) *Makromol. Chem.* **193**: 687.
20. Kricheldorf HR, Schwarz G (1987) *Makromol. Chem.* **188**: 1281.
21. Kwolek SL, Luise RR (1986) *Macromolecules* **19**: 1789.
22. Domb AJ, Langer R (1987) *J. Polym. Sci., Part A: Polym. Chem.* **25**: 3373.
23. Yoda N (1959) *Makromol. Chem.* **32**: 1.
24. Buckingham J (1982) *Dictionary of Organic Compounds* Chapman and Hall, New York.
25. Lide DR (1997) *CRC Handbook of Chemistry and Physics* CRC Press, Boca Raton.