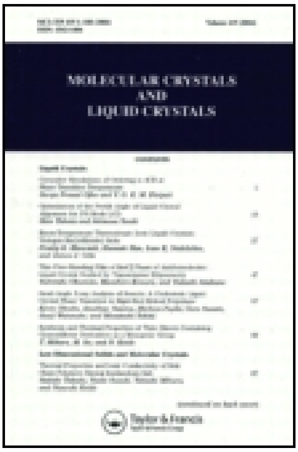


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Polyurethanes Containing Dioxybenzylidenecyanoacetate as a NLO-Chromophore and Their Properties

Ju-Yeon Lee [a] , Eun-Ju Park [a] , Tae-Sun Kang [a] , Hoosung Lee [b] , Kukro Yoon [b] , Nami Byun [b] , Bum Ku Rhee [c] , Changsoo Jung [c] & Mi Young Joo [c]

[a] Department of Chemistry, Inje University, 607 Aebang-dong, Kimhae, 621-749, Korea

[b] Department of Chemistry, Sogang University, Mapoku, Seoul, 121-742, Korea

[c] Department of Physics, Sogang University, Mapoku, Seoul, 121-742, Korea

Version of record first published: 29 Oct 2010

To cite this article: Ju-Yeon Lee, Eun-Ju Park, Tae-Sun Kang, Hoosung Lee, Kukro Yoon, Nami Byun, Bum Ku Rhee, Changsoo Jung & Mi Young Joo (2002): Synthesis of Polyurethanes Containing Dioxybenzylidenecyanoacetate as a NLO-Chromophore and Their Properties, Molecular Crystals and Liquid Crystals, 377:1, 269-272

To link to this article: http://dx.doi.org/10.1080/713738562

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 269-272
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290089059

Synthesis of Polyurethanes Containing Dioxybenzylidenecyanoacetate as a NLO-Chromophore and Their Properties

JU-YEON LEE[a,*], EUN-JU PARK[a], TAE-SUN KANG[a],
HOOSUNG LEE[b], KUKRO YOON[b], NAMI BYUN[b],
BUM KU RHEE[c], CHANGSOO JUNG[c] and MI YOUNG JOO[c]

[a,*]*Department of Chemistry, Inje University, 607 Aebang-dong,*
Kimhae 621-749, Korea,
[b]*Department of Chemistry, Sogang University, Mapoku,*
Seoul 121-742, Korea and
[c]*Department of Physics, Sogang University, Mapoku, Seoul 121-742, Korea*

Methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate **3** was prepared and condensed with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate to yield polyurethanes **4** and **5** containing the NLO-phore dioxybenzylidenecyanoacetate group. The resulting polyurethanes **4-5** were soluble in common organic solvents. Polymers **4-5** showed a thermal stability up to 290°C in TGA thermograms with T_g values in the range of 97-102°C in DSC thermograms. The SHG coefficients (d_{33}) of poled polymer films were 4.7×10^{-9} esu.

Keywords 2,4-Toluenediisocyanate; Glass transition temperature; Atomic force microscopy (AFM) image; SHG coefficient (d_{33})

*Correspondence to JU-YEON LEE, Tel.: +82-55-320-3221; Fax: +82-55-321-9718; E-mail: chemljy@ijnc.inje.ac.kr.

INTRODUCTION

Nonlinear optical (NLO) polymers have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc. One of the current challenges is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization have been proposed. One is to use crosslinking method and the other is to utilize high T_g polymers such as polyimides [1]. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. In this work we prepared novel polyurethanes containing dioxybenzylidenecyanoacetate group, which is presumably effective NLO-chromophore. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and second order NLO activity.

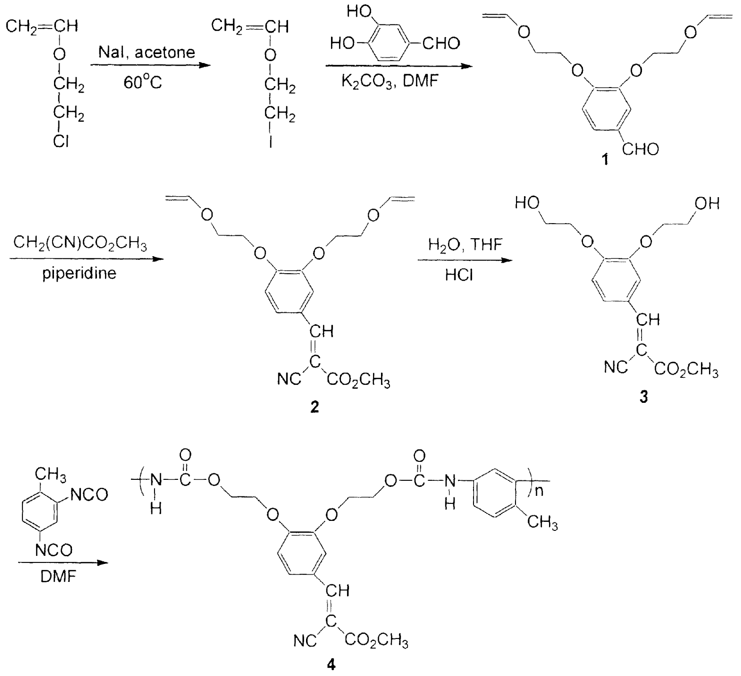
EXPERIMENTAL

Polyurethanes **4** and **5** were prepared according to a literature procedure [2]. The alignment of the NLO-chromophore of the polymers was carried out by corona poling method (110°C, 6 kV, 30 min). Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode which measures topography. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [4].

RESULTD AND DISCUSSION

Synthesis and characterization of NLO polyurethanes 4-5

Methyl 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**) was pre pared by the condensation reaction of 3,4-di-(2'-vinyloxyethoxy)benzal dehyde (**1**) with methylcyanoacetate. Polymers **4** and **5** were prepared by the polyaddition between a diol **3** and 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate. The chemical structure of the compounds was confirmed by ^{1}H NMR, IR, and elemental analysis. The signal at 8.77-9.04 ppm of the ^{1}H NMR spectra assigned to the amine proton indicates the formation of urethane linkage.



SCHEME 1. Synthetic method of polymer **4**.

Properties of polyurethanes **4** and **5**

The polymers **4-5** were soluble in common solvents such as acetone and DMF. Polymers **4-5** showed a thermal stability up to 290°C with T_g values around 97-102°C. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled at 110°C and 6 kV of corona voltage. The UV-Vis absorption spectra of the polymer samples before and after the poling were recorded. After the poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectra of polymers **4-5** exhibited a decrease in absorption due to birefringence. AFM images show that the surface of the film sample is extremely flat and clean. However, this good quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which were aligned the poling direction. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser [3]. The SHG coefficient d_{33} was calculated through the method developed by Herman et al [4]. The SHG measurements revealed a d_{33} value of 4.7×10^{-9} esu for polymer **4**.

ACKNOWLEDGEMENTS

This work was supported by Korea Research Foundation Grant

REFERENCES

[1] M. W. Becker, L. S. Sapochak, R. Ghosn, L. R. Dalton, Chem. Mater. **6**, 104 (1994).
[2] J.-Y. Lee, E.-J. Park, Polym. Int'l. in press (2001).
[3] P. D. Maker, R. W. Terhune, M. Nisenoff, C. M. Savage, Phy. Rev. Lett. **8**, 21 (1962).
[4] W. N. Herman, L. M. Hayden, J. Opt. Soc. Am. B **12**, 416 (1995).