Polymer Bulletin 41, 417–423 (1998)

Polymer Bulletin

A new class of poly(1,6-heptadiyne)-based photorefractive materials by metathesis polymerization

Ji-Hoon Lee[2], In Kyu Moon[1], Hwan Kyu Kim[1,*], Sam-Kwon Choi[2]

[1] Department of Macromolecular Science, Hannam University, 133 Ojung-Dong,
Daeduck-Gu, Taejon 300-791, Korea
[2] Department of Chemistry, Korea Advanced Institute of Science and Technology,
371-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, Korea

Received: 1 June 1998/Revised version: 27 July 1998/Accepted: 5 August 1998

SUMMARY: We utilized the first metathesis reaction to synthesize a new type of photorefractive polymers that contain both a carbazole moiety as a hole transporter and NLO chromophores. These polymers have a long tail band at above 700 *nm*, indicating the formation of intramolecular charge transfer complexes between the carbazole groups and the conjugated double bonds in the polymer backbone. Also, these polymers show two maximum values of photocurrent around 350 and 700 *nm*. The electro-optic coefficient (r_{33}) at the wavelength of 1.3 μm for polymer thin films poled around the 85°C were in the range of 1.6 ~6.3 *pm/V*. The hyperpolarizabilities, $<\gamma>$, of the resulting polymers were *ca.* 2.9 x 10^{-32} *esu.* at the incident wavelength of 1.907 μm.

INTRODUCTION

Materials exploring a photorefractive effect are main candidates for numerous applications, including high-density optical data storage, optical image processing, phase conjugated mirrors and laser, dynamic holography, optical computing, pattern recognition, etc. (1~3). Photocharges generated in a medium by a spatially modulated light intensity migrate through drift and/or diffusion processes and eventually become trapped, establishing an internal, space charge field which, in turn, modulates the material's refractive index via the linear electrooptic effect-the Pockels effects. To manifest photorefractive effect, the polymer must possess a photocharge generator, a charge transporter, a charge trapping center, and a nonlinear optical chromophore. In an earlier period, most of the initially reported polymeric photorefractive materials fell into one of two following composite systems (2): [i] Second-order nonlinear optical polymers doped with charge transporting agents [ii] Photoconductive polymers doped with second-order nonliner optical chromophores. These polymeric composite systems have a merit of the ease of preparation. However, they also have some problems such as phase separations and the instability of electro-optical activities. To overcome these problems, multifunctional polymers with all of the four functionalities (NLO-chromophore, charge generator, charge transfer, trapping center) covalently attached to the polymer backbone were synthesized. Moreover, the synthetic approach to multifunctional polymes offers further opportunity to explore new structures rationally for the photorefractive effects, while it is difficult in composite systems. Very recently, we have utilized the first metathesis reaction to synthesize a new type of photorefractive polymers, based on poly(1,6-heptadiyne) derivatives, that contain both a carbazole moiety as a hole transporter and NLO chromophores attached to π -conjugated backbones as to in Scheme 1. Previously, we reported that these

---

[*] Corresponding author

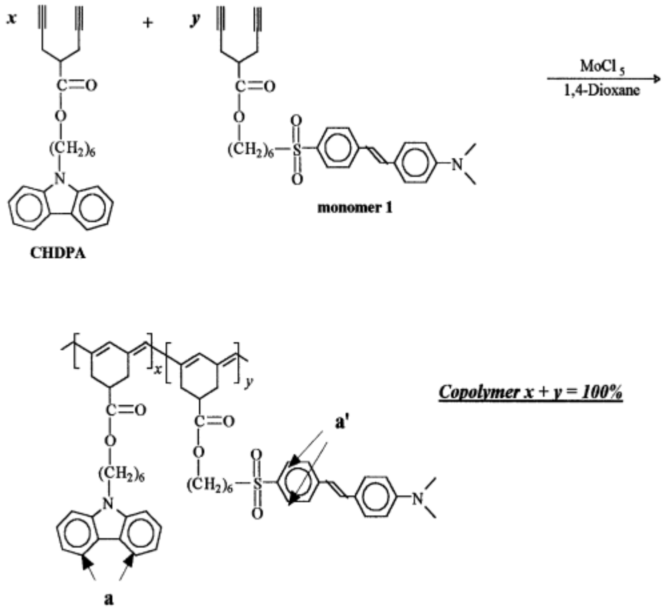
cyclopolymerizations of 1,6-heptadiyne derivatives were tolerent of a wide variety of polar functional groups based on π-conjugated cyclic units in a polymer main chain. Therefore it was used to generate a variety of functionalized poly(1,6-heptadiyne)s having various functional groups such as mesogens, electron donor or acceptor, nonlinear optical (NLO) chromophores, etc. (4~12). In this paper, we report the synthesis and optical properties of new photorefractive polymers based on poly(1,6-heptadiyne) derivatives by metathesis catalysts.

EXPERIMENTAL

Synthesis

Hole transporter, second-order nonlinear optical chromophore, 1,6-heptadiyne derivatives, and copolymerization were carried out as cited in references (8, 11). The synthetic schemes of the copolymer are shown in Scheme 1.

Scheme 1



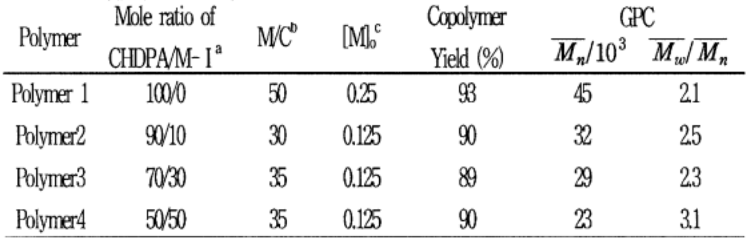
RESULTS AND DISCUSSION

Photorefractive polymers are multifuctional polymers that also possess photoconductivity and electro-optical activity. To manifest photorefractive effect, the polymer must possess a photocharge generator, a charge transporter, a charge trapping center, and a nonlinear optical chromophore (2, 13). Very recently, we develop novel photorefractive polymers based on the previous works for the photoconductivity of poly(1,6-heptadiyne) derivatives containing a carbazole moiety (8) and electro-optic activity of poly(1,6-heptadiyne) derivatives containing NLO chromophores (9, 11). Herein, all functional groups is covalently linked to the polymer backbone. Scheme 1 outlines the copolymerization of a chromophoric monomer 1 (M- I) with (*N*-carbazoyl-*n*-hexyl) dipropargyl acetate (CHDPA) by $MoCl_5$. The copolymerization of

CHDPA with monomer 1 exhibits very effective catalytic activity by $MoCl_5$ catalyst. In Table 1, the results for the copolymerization are summarized. The molecular weights of the resulting polymers were estimated by gel-permeation chromatography (GPC) to be in the range $\overline{M_n}$ =2.3 X 10^4 to 4.5 X 10^4 and polydispersities of the resulting polymers were in the range of 2.1 ~ 3.1.

The analysis of the resulting copolymers were established by ^{1}H-NMR, infrared and UV-visible spectroscopies. Table 1 shows the copolymerization results by metal catalysts.

Table 1. The results for copolymerization by $MoCl_5$.



Polymer	Mole ratio of CHDPA/M- I[a]	M/C[b]	$[M]_0$[c]	Copolymer Yield (%)	GPC $\overline{M_n}/10^3$	GPC $\overline{M_w}/\overline{M_n}$
Polymer 1	100/0	50	0.25	93	45	2.1
Polymer2	90/10	30	0.125	90	32	2.5
Polymer3	70/30	35	0.125	89	29	2.3
Polymer4	50/50	35	0.125	90	23	3.1

a. monomer 1 ; b. Mole ratio of monomer to catalyst. ; c. Initial monomer concentration.

The IR spectra of the polymer showed no absorption peaks at 3290 and 2140 cm^{-1}, which are expected to be present for the acetylenic carbon-hydrogen bond stretching and carbon-carbon triple bond stretching in the monomer, respectively. Like homopolymerization of CHDPA, a $MoCl_5$ catalyst for the copolymerization of CHDPA with monomer 1 was very effective. IR spectra of all copolymers shows no absorption at 3290 cm^{-1} which are expected to be present for the acetylenic hydrogen-carbon stretching of the monomers, and, in addition, as the mole fraction of monomer 1 was increased, the absorbance at near 1595 cm^{-1} was increased, which the peak is due to the aromatic C=C stretching on the stilbene moiety of monomer 1 (see Figure 1). Also, the absorptions for the SO_2 unit at *ca*. 1378 cm^{-1} and aromatic C-H of carbazole unit at *ca*. 750 and 724 cm^{-1} were detected.

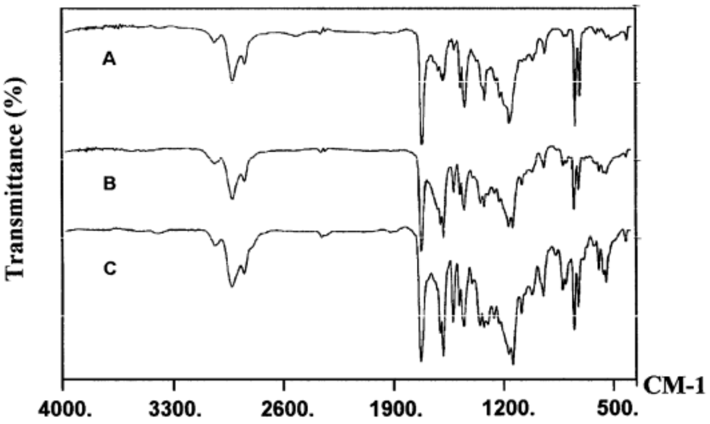


Figure 1. IR spectra of polymer 1 (A), polymer 2 (B), and polymer 3 (C).

Also, the ^{1}H-NMR spectra of both the CHDPA, the poly(CHDPA) (polymer 1) and copolymers are shown in Figure 2. The ^{1}H-NMR spectrum of the CHDAP appeared in 1.3-1.9 *ppm* [m, 8H, -$(CH_2)_4$-], 1.96 *ppm* [t, 2H, ≡ CH], 2.5 *ppm* [d, 4H, -$CH_2C \equiv C$], 2.7 *ppm* [m, 1H, -CH], 4.2 *ppm* [t, 2H, -CO_2CH_2-], 4.45 *ppm* [t, 2H, -CH_2N], 7.1-8.0 *ppm* [m, 16H, aromatic]. As the polymerization proceeded, an acetylenic proton peak at around 1.99 *ppm* disappeared and new vinylic proton peaks appeared in the aromatic region. Also, the mole ratios of the resulting copolymers were determined by ^{1}H-NMR analysis, where the integration of phenyl protons of carbazole at 7.97 *ppm* and one of the phenyl protons of NLO chromophore at 7.69 *ppm* were compared (see Figure 1 and Table 2). As a result, it was found that the copolymers including polymer 2, polymer 3, and polymer 4, were polymerized nearly quantitatively as a monomer feed.

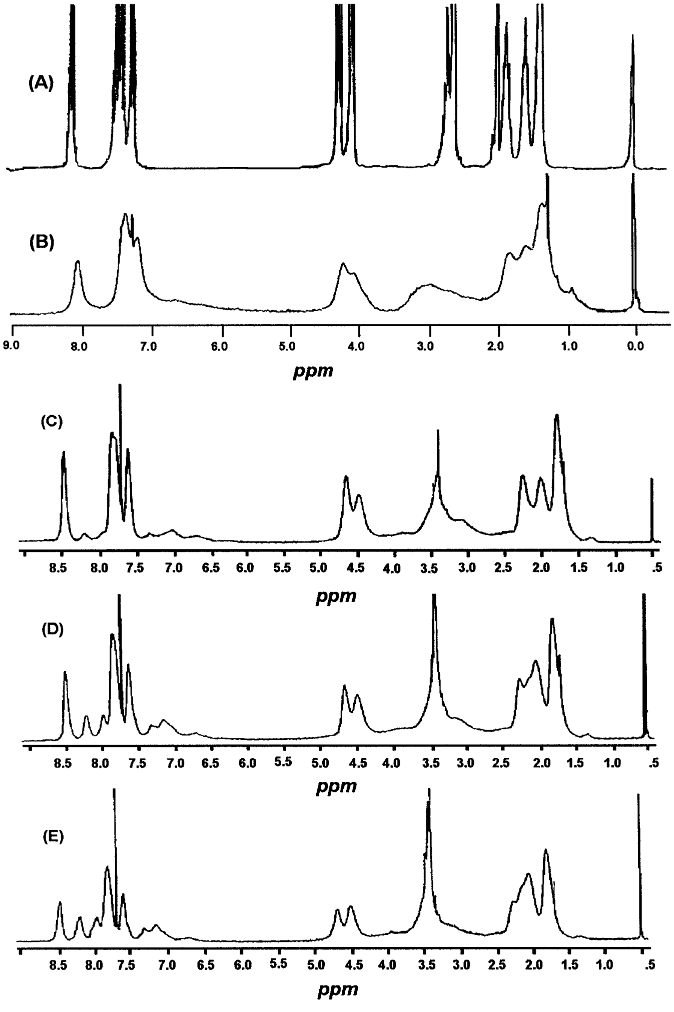


Figure 2. ^{1}H-NMR spectra of the CHDPA (A), polymer 1 (B), polymer 2 (C), polymer 3 (D), and polymer 4 (E) in $CHCl_3$.

Table 2. Copolymer Composition by ^{1}H-NMR

	Monomer feed (calcd)	^{1}H-NMR data (found)[a]
	CHDPA / M-I	
	(phenyl protons, H_a, of carbazoles) / (phenyl protons, $H_{a'}$, of NLO chromophores)	
Polymer 2	90/10	91/9
Polymer 3	70/30	68/32
Polymer 4	50/50	55/45

a. Determined by integration of phenyl protons of carbazoles (H_a, 7.97 *ppm*) and phenyl protons of NLO chromophores ($H_{a'}$, 7.67 *ppm*) (see Scheme 1)

Figure 3 shows the UV-visible spectra of the monomer 1 and copolymers. These polymers have a long tail band at above 700 *nm*, indicating the formation of intramolecular charge transfer complexes between the carbazole groups and the conjugated double bonds in the polymer backbone. Also, these polymers show two maximum values of photocurrent around 350 and 700 *nm*. The former one might be due to the carbazole groups and the latter might be based on the photodetrapping in shallow electron traps and charge carrier generation in the charge transfer band.

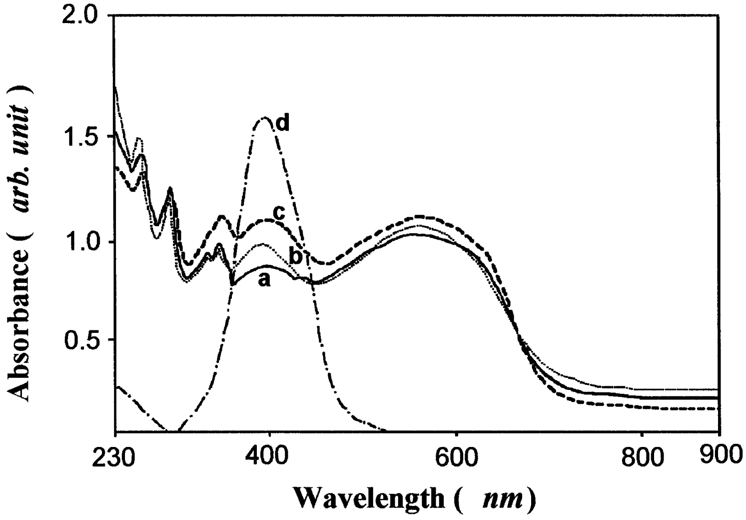


Figure 3. UV-visible spectra of polymer 1 (a), polymer 2 (b), polymer 3 (c), and the monomer 1 (d) in $CHCl_3$.

Poly(CHDPA) containing a carbazole moiety as a hole transporter was completely soluble in various organic solvents such as chloroform, THF, 1,4-dioxane, etc., and also all copolymers of various mole ratio was relatively well soluble in common organic solvents. However, the homopolymer of monomer 1 having NLO chromophore was insoluble in any organic solvents. These copolymers were easily cast on ITO glass plate or quartz plate to give violet, shiny thin films. The polymers were dissolved in 1,1,2-trichloroethane (TCE) or THF at a concentration of range of 5 to 15 *wt*. % depending on the desired film thickness.

The thermal stability of the resulting polymers was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The initial decomposition temperature of the poly(CHDPA) exhibited at near 303 °C (scanning rate = 10°C/*min.* in N_2), while that of copolymer decrease according to the mole ratio increasement of monomer 1.

Optical-quality thin films (2~3 *μm*) of poly(1,6-heptadiyne)-based photorefractive polymers were prepared by spin-coating the polymer solutions in TCE onto ITO glass substrate, and then aluminum or gold electrode were evaporated on top of the polymer film. A film was slowly heated to 85°C and then a positive voltage was applied to the top electrode and ITO was grounded. After 10 *min*, the heater and the voltameter were turned off sequentially. Table 3 shows the measured linear and electro-optic coefficients of polymer films at 1.3 μm. The optimized r_{33} value for polymer 2, polymer 3, and polymer 4 were 1.6, 3.6, and 6.3 *pm*/V, respectively.

Table 3. Linear and Nonlinear Optical Data for Polymers

Polymer	λ_{max} (*nm*) NLO chromophre	λ_{max} (*nm*) Backbone	n^a (1.3μm)	V_p^b (V/μm)	r_{33} (*pm*/V)^c (1.3μm)
Polymer 2	394	548	1.660	100	1.6
Polymer 3	392	550	1.661	114	3.6
Polymer 4	396	550	1.664	161	6.3

a. Indices of refraction were determined from waveguiding experiments.;
b. Electric field during poling; c. Electro-optic coefficient

The intensity of DFWM (degenerate four-wave mixing) signal for the poly(CHDPA) increased linearly with intensity of incident beam. From the direct comparison between the intercepts of Y axis of the poly(CHDPA) and the carbon disulfide reference, the $\chi^{(3)}$ values of the polymers were obtained. The hyperpolarizabilities, $<\gamma>$, of the poly(CHDPA) were obtained from aforementioned equation (14).

The $<\gamma>$ values of poly(CHDPA) was *ca.* 2.9 X 10^{-32} *esu.* (0.1 *M* in THF) at the incident wavelength of 1.907 *μm.*

At present, the photorefractive properties of the polymer are being studied by the four-wave mixing (FWM) and two-beam coupling (2BC) techniques. Also, the study of the optimum conditions to attain higher EO coefficient and thermal stability is in progress.

Acknowledgment H. K. Kim greatly acknowledges that this work was financially supported by Korean Science and Engineering Foundation (No. 96-0300-10-01-3).

REFERENCE

1. Gibson HH and Skotheim TA (1986) Handbook of Conducting Polymer ; New York and Basel, Switzerland, 1:405.
2. Moerner WE and Silence SC (1994) Chem. Rev. 1994, 94:127.
3. Ducharme S, Scott JC, Twieg RJ, Moerner, WE (1991) Phys. Rev. Lett., 66:1846.
4. Ryoo MS, Lee WC, and Choi SK (1990) Macromolecules, 23:3029.
5. Kim YH, Gal YS, Kim UY, and Choi SK (1995), Macromolecules, 21:1991.
6. Cho OK, Kim YH, and Choi SK (1990) Macromolecules, 23:12.

7. Jang MS, Kim UY, Kang YS, and Choi SK (1990), Macromolecules, 23:4135.
8. Lee JH, Park JW, Oh JM, and Choi SK (1995) Macromolecules, 28:377.
9. Lee HJ, Won YH, Kang SJ, Choi, SK, and Kim HK (1996), J. Polym. Sci., Part A: Polym. Chem. Ed., 34:2333.
10. Jin SH, Kim SH, Cho HN, and Choi SK (1991) Macromolecules, 24:6050.
11. Lee HJ, Oh JM, Choi SJ, Kim HK, and Choi SK (1994) Polym. Bull. 32:433.
12. Lee HJ, Kang SJ, Kim HK, Cho HN, Park JT, and Choi SK (1995) Macromolecules, 28:4638.
13. Peng Z, Gharavi AR, and Yu L (1997) J. Am. Chem. Soc. 119:4622.
14. Prasad PN and Williams DJ (1991) Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley Interscience, New York.