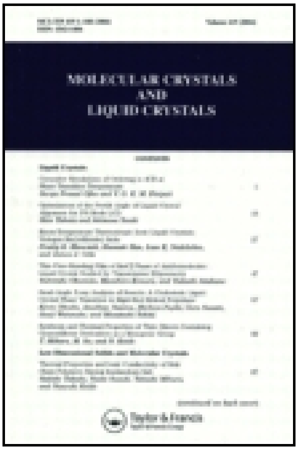

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A New Class of Poty(1,6-heptadiyne)-Based Photorefractive Materials by Metathesis Polymerization

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A New Class of Poly(1,6-heptadiyne)-Based Photorefractive Materials by Metathesis Polymerization

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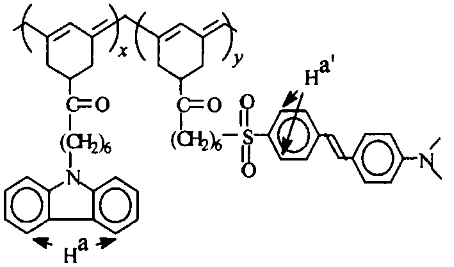
ABSTRACT We utilized the first metathesis reaction to synthesize a new type of photorefractive polymers that contain both a carbazole moiety as a hole transporter and NLO chromophores, attached to π-conjugated backbones. These polymers show two maximum values of photocurrent around 350 and 700 *nm*. The electro-optic coefficient (r_{33}) of the poled polymer films measured at the wavelength of 1.3 μm was in the value of 10.1 *pm/*V. The nonresonat values of the third-order NLO coefficient, $\chi^{(3)}$, of the resulting polymers were found to be 2.9 x 10^{-32} *esu.* at the incident wavelength of 1.907 μm.

Keywords: photorefractive polymer, poly(1,6-heptadiyne), 2nd- order NLO coefficient, photocurrent

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..[1,2] Considerable progress has been made in the research on phtorefractive polymers and composites, since the first polymeric photorefractive material was based on a second-order nonlinear optical polymer doped with a charge transporting agent and a photocharge generation sensitizer only six years ago. To manifest photorefractive effect, the polymer must possess a photocharge generator, a charge transporter, a charge trapping center, and a nonlinear optical chromophore.[6] Very recently, we 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 in Scheme 1. Since cyclopolymerization of 1,6-heptadiyne derivatives are tolerant of a wide variety of polar functional groups based on π-conjugated cyclic units in polymer main chain, it can be 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.. In this paper, we report the synthesis and optical properties of new photorefractive polymers based on poly(1,6-heptadiyne) derivatives by metathesis catalysts.[3-5]

SCHEME 1



$x + y = 100$ %
Homopolymer ; $x = 100, y = 0$
Copolymer 1 ; $x = 90, y = 10$
Copolymer 2 ; $x = 70, y = 30$
Copolymer 3 ; $x = 50, y = 50$

RESULTS AND DISCUSSION

We developed novel photorefractive polymers based on the previous works for the photoconductivity of poly(1,6-heptadiyne) derivatives containing a carbazole moiety and electro-optic activity of poly(1,6-heptadiyne) derivatives containing NLO chromophores (Monomer 1). [8] The copolymerization of CHDPA with Monomer 1 (M-1) exhibits very effective catalytic activity by $MoCl_5$ catalyst. In table 1, the results for the copolymerization were summarized. The maximum content of Monomer 1 having NLO chromophore in copolymer was limited by the solubility of the resulting polymeric products. In other words, as the content of Monomer 1 increased, the solubility of the resulting copolymers decreased. Presumably, it is due to a high polarity of NLO chromophore, which could be act as a deactivator for transition metal catalysts. The chromophore monomers were polymerized with ethyl dipropargy (diethoxyphosphoryl) acetate (TDPA). The copolymerization (CP-TDPA) of Monomer 1 with TDPA obtained for the moderate polymer yields and good soluble polymers in various organic solvents. The soluble copolymer could be prepared to about 50 *mol* % of NLO chromophore-containing Monomer 1.

TABLE 1. Copolymerization of the Monomer 1 with CHDPA by $MoCl_5$.

Mole ratio of CHDPA/M-1	M/C[a]	$[M]_0$[b]	Yield (%)	GPC		Copolymer composition ^{1}H-NMR data (found)[c]
				$M_n/10^3$	M_w/M_n	CHDPA(H^a) / M-1($H^{a'}$)
100/0	50	0.25	93	45	2.1	
90/10	30	0.125	90	32	2.5	91/9
70/30	35	0.125	89	29	2.3	68/32
50/50	35	0.125	90	23	3.1	55/45
0/100	25	0.125	-			

[a] Mole ratio of monomer to catalyst. ; [b]. Initial monomer concentraion. ;

[c] Determined by integration of phenyl protons of carbazoles (H^a, 7.97 *ppm*) and phenyl protons of NLO chromophores ($H^{a'}$, 7.67 *ppm*).

Herein, all functional groups is covalently linked to the polymer backbone. The analysis of the resulting copolymers were established by ^{1}H-, ^{13}C-NMR, infrared and UV-visible spectroscopies. The UV-visible spectra of the Monomer 1 and copolymers (see Figure 1). 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 an latter might be based on the photodetrapping in shallow electron traps and charge carrier generation in the charge transfer band. The r_{33} of CP-TDPA bearing 4-amino-4'-sulfone stilbene chromophore poled at the 161 V/μm was observed at the highest value of 10.1 *pm*/V.[7] The $<r>^{(3)}$ values of poly(CHDPA) was 1 x 10^{-11} *esu.* at the incident wavelength of 1.907 μm.

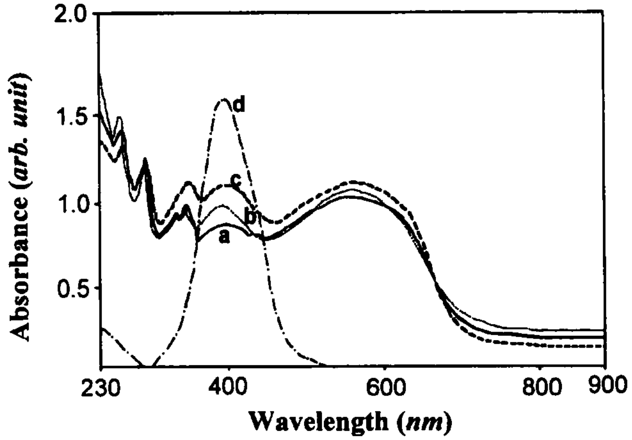


FIGURE 1. UV/vis. spectra of 10 *mol* % copolymer 1(a), 30 *mol* % copolymer 2(b), 50 *mol* % 3(c), and the M-1 (d). The copolymer spectra were taken in thin films coated on quartz substrate and the M-1 spectrums was taken in $CHCl_3$ solution.

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