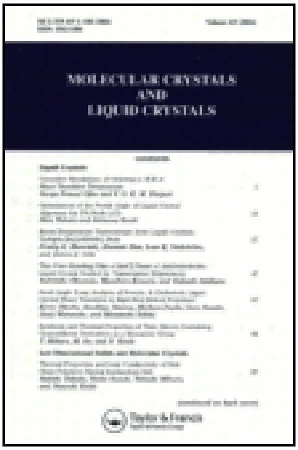

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Synthesis and Characterization of Poly(1,6-Heptadiyne) Derivatives Containing Alkylsilyloxy Groups

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Synthesis and Characterization of Poly(1,6-Heptadiyne) Derivatives Containing Alkylsilyloxy Groups

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Poly(1,6-heptadiyne) derivatives containing side chain alkylsilyloxy group were synthesized by metathesis polymerization. It was found that the catalytic activity of Mo-based catalysts was greater than that of W-based catalysts. Polymerization of these monomers gave to the conjugated polyenes containing cyclic repeating units in the polymer backbone. The resulting polymers exhibited good thermal property and solubility in common organic solvents and were easily spin-coated on ITO coated substrate.

Keywords poly(1,6-heptadiyne); conducting polymer; metathesis polymerization

INTRODUCTION

π-conjugated polymers such as polyacetylene derivatives[1], poly(aromatic vinylene)[2], Polythiophene[3] etc., have been extensively studied for potenial application in electronic and photonic devices. However, the practical application has been limited since the π-conjugated polymers are generally unstable under ambient conditions and insoluble in organic solvents. To increase the processability and provide the various functionalities of polyacetylenes, with a minimum decrease of conductivity as a trade-off, we have introduced various types of substitutents at the 4-position of 1,6-heptadiyne. The present articles deals with the synthesis and characterization of a novel class of π-conjugated poly(1,6-heptadiyne) derivatives containing alkylsilyloxy groups by metathesis polymerization. Alkylsilyloxy groups give unique properties, which include the good flexibility, solubility, gas permeability and adhesion to the ITO substrate. The characterization and physical properties of the resulting polymers are also discussed.

EXPERIMENTAL

Diethyldipropargyl malonate (DEDPM), dipropargylmalonic acid, dipropargylacetic acid and dipropargylacetyl chloride were synthesized according to the literature [4]. A mixture of 3-chloropropyltrimethylsilane (12g, 80 mmol), diprppargylacetic acid (10.2 g, 87 mmol), K_2CO_3 (12 g, 87 mmol) and DMF (150 ml) is gently refluexed for 10 hrs. The reaction mixture was cooled to room temperature and poured into water, and extracted with diethyl ether. The organic layers was dried over anhydrous $MgSO_4$. The volatile components were removed in vacuo. The resulting viscos oil was distilled (88-100°C/0.5 mmHg) to give a 4-(carboxy-3-trimethylsilyl-1-propyl)-1,6-heptadiyne (Monomer-1) (14.5 g, 77%) : ^{1}H-NMR ($CDCl_3$, δ ppm) 4.1 (t, 2H, OCH_3), 2.70 (m, 1H, CH), 2.59 (dd, 4H, CH_2C), 2.05 (t, 2H, CH), 1.59 (m, 2H, OCH_2CH_2), 0.51 (m, 2H, CH_2Si), 0.01 (s, 9H, $SiCH_3$) Monomer-2 was synthesized by the reaction of dipropargylmalonyl chloride with the 3-trimethylsilyl-1-propanol in the presence of pyridine using the diethyl ether solvent. The resulting product was purified by the flash column using hexane as an eluent to give 12.5 g (83 %) of product. ^{1}H-NMR ($CDCl_3$, δ ppm) : 4.12 (t, 4H, OCH_2), 2.96 (d, 4H, CH_2C), 1.98 (t, 2H, CH), 1.58 (m, 4H, OCH_2CH_2), 0.49 (m, 4H, CH_2Si), -0.04 (s, 18H, $SiCH_3$) The polymerization of the monomers was carried out by metathesis catalysts such as $MoCl_5$, WCl_6 and $EtAlCl_2$, $(n\text{-}Bu)_4Sn$ as a cocatalysts. The polymerization procedure was the same as reported elsewhere [4].

RESULTS AND DISCUSSION

In order to investigate the substitutent effect on the polymerization behavior, we introduced the single and paired substitutents at the 4-position of 1,6-heptadiyne. The polymerization of the Monomer-1 and -2 were carried out with $MoCl_5$-, WCl_6-based catalysts and the results are summarized in TABLE 1. The catalytic activity of $MoCl_5$ was greater than that of WCl_6. A highly Lewis-acidic WCl_6-based catalyst, which showed excellent catalytic activity for the polymerization of phenylacetylene, exhibited poor catalytic activity for the monomers containing a polar functional group such as ester group. The number-average molecular weight (Mn) and polydispersity of the resulting polymers were found in the range of 8.7 ~ 126.4 x 10^3 and 1.7 ~ 4.2, respectively. The resulting Polymer-2 has higher degree of polymerization than that of Polymer-1. The paired substitutents in 1,6-heptadiyne are more favorable than single substitutent monomer in the transition state for cyclopolymerization. As the polymerization proceeded, acetylenic proton peaks of the monomers at 2.1 ppm disappeared, and a new broad peaks due to the protons on the conjugated vinylic proton peaks appeared at 6 ~ 7 ppm. UV-visible absorption spectra of the polymer-1 and 2 in THF solvent exhibit a characteristic broad peak at 430 ~ 630 nm, which is due to the π-π^* transition of conjugated polymers. The resulting polymers containing alkylsilyloxy side chain exhibited good solubility behavior in common organic solvents such as chloroform, THF, *p*-dioxane and DMF etc., and easily spin cast onto the ITO coated glass substrate. The obtained films were extremely uniform in thickness over the whole area of substrate and were optically clear without any defects. The electrical conductivity of iodine-doped polymers were 10^{-2} to 10^{-4} S/cm. TGA suggests that the polymer-I is stable up 286°C and 82.7 % by weight was lost below 586 °C.

Table 1. Polymerization of monomers by transition metal catalysts

Sample	Catalyst. System (mole ratio)	Polymer yield	Mn x 10^3	Mw/Mn
Monomer-1	$MoCl_5$	94	27.4	2.73
Monomer-1	WCl_6	23	8.7	4.2
Monomer-2	$MoCl_5$	98	126.4	2.34
Monomer-2	$MoCl_5$-$EtAlCl_2$ (1:4)	98	102.3	2.87

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