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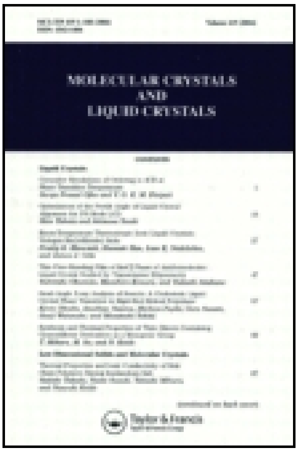

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Synthesis and Solid-State Polymerization of 4-(Dimethylamino)phenylbutadiyne Derivatives and Their Charge-Transfer Complexes

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Synthesis and Solid-State Polymerization of 4-(Dimethylamino)phenylbutadiyne Derivatives and Their Charge-Transfer Complexes

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Five urethane derivatives of 8-[4-(dimethylamino)phenyl]octa-5,7-diyn-1-ol were synthesized. They could be polymerized in the solid state to give conjugated backbones although structural regularity seemed to be not so high. Formability of charge-transfer (CT) complex of one of the urethane derivatives and bis[4-(dimethylamino) phenyl]butadiyne as a reference compound with acceptors, such as 1,4-benzoquinone, 2,4,7-trinitrofluorenone etc., were investigated by solution mixing and powder co-grinding methods. In some cases, the CT complex formability was changed by the preparation method.

Keywords Charge-transfer complex; conjugated polymer; donor; polydiacetylene; solid-state polymerization

1. Introduction

Conjugated polymers are often recognized as conducting polymers. However, polydiacetylene obtained by solid-state polymerization of butadiyne monomers [1] has been exception because its high crystallinity avoids immersing dopant molecules into the crystals and effective doping is difficult [2]. On the other hand, charge-transfer (CT) complexes such as tetrathiafluvalene-tetracyanoquinodimethane (TTF-TCNQ) have high crystallinity and high conductivity [3]. Thus, if we combine these two systems, i.e., conjugated polymers and CT complexes, interesting electronic properties may appear. Our strategy is as follows: First, butadiyne derivatives with a donor (or an acceptor) moiety directly bound to the butadiynyl group are synthesized. Second, the monomers are mixed with acceptor (or donor) molecules to form the CT complexes. Finally, the CT-complex monomers are polymerized in the solid state. However, synthesis of solid-state polymerizable butadiyne monomers directly substituted by one or two aromatic groups is quite difficult, and several attempts should be required for the final goal. In this study as one step of this approach, we synthesized butadiyne derivatives directly substituted by a 4-(dimethylamino)phenyl group as donor-attached monomers. Their solid-state polymerizability and CT-complex formability with acceptors were investigated.

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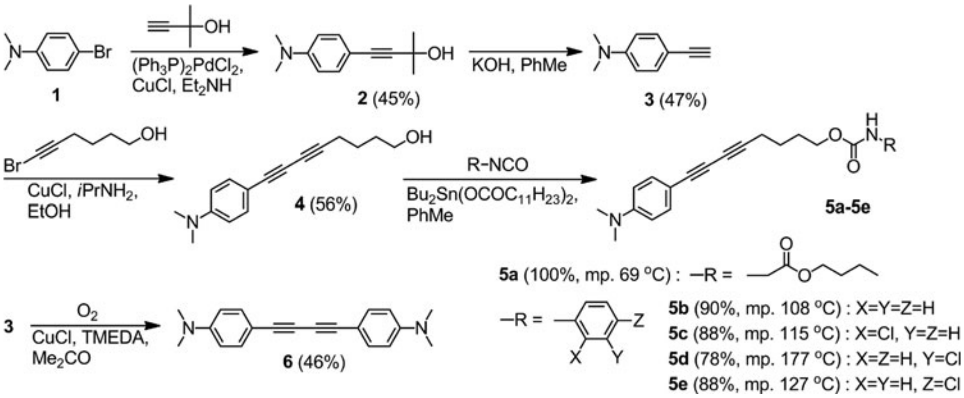

Figure 1. Synthesis scheme of 4-(dimethylamino)phenylbutadiyne derivatives.

2. Experimental

4-(Dimethylamino)phenylbutadiyne derivatives **5a**–**5e** and the reference compound **6** were synthesized according to Fig. 1. The monomer melting points measured by a SII DSC 6220 differential scanning calorimeter are also shown in Fig. 1. Their structures were identified by ^{1}H- and ^{13}C-NMR spectra, IR spectra and elemental analyses. NMR spectra were obtained using JEOL ECX-400 spectrometers, and IR spectra were recorded on a Horiba FT-210 spectrometer. The data for **5a** as a representative compound are as follows: ^{1}H-NMR ($CDCl_3$, δ) 0.94 (3H, t, J = 7.2 Hz), 1.38 (2H, tq, J = 7.5, 7.2 Hz), 1.59–1.68 (4H, m), 1.77 (2H, m), 2.40 (2H, t, J = 7.0 Hz), 2.97 (6H, s), 3.96 (2H, d, J = 5.0 Hz), 4.12 (2H, t, J = 6.3 Hz), 4.16 (2H, t, J = 6.6 Hz), 5.15 (1H, broad t), 6.59 (2H, d, J = 9.0 Hz), 7.35 (2H, d, J = 9.0 Hz); ^{13}C-NMR ($CDCl_3$, δ) 13.59, 18.97, 19.27, 24.79, 28.06, 30.50, 40.01, 42.68, 64.66, 65.26, 66.13, 72.21, 76.51, 82.65, 108.20, 111.61, 133.69, 150.36, 156.44, 170.09; IR (KBr) 3273, 3153, 2962, 2871, 2239, 2133, 1743, 1720, 1604, 1522, 1437, 1358, 1333, 1198, 1161, 1066 cm^{-1}; Found: C, 69.32; H, 7.67; N, 6.92%. Calcd for $C_{23}H_{30}N_2O_4$: C, 69.32; H, 7.59; N, 7.03%.

Solid-state polymerization was examined by UV irradiation at 254 nm from a 4-W lamp (UVP, UVG-11). Conversion to the polymer by UV irradiation for 3 h was estimated from heat of melt, measured using DSC, for the monomer contained in the polymerized samples. The CT complexes were prepared by two methods, i.e., solution mixing and powder co-grinding [4]. In the solution mixing method, monomer solution was mixed with acceptor solution, and solvent was evaporated. Solvent used were chloroform or THF or acetonitrile. In the powder co-grinding method, monomer and acceptor crystals were mixed and well ground using agate mortar and pestle. Mixing molar ratios of monomer and acceptor molecules were 1:1 for **5a** and 1:2 for **6**. UV-visible-NIR diffuse reflectance spectra of the solid samples were recorded using a Jasco V-570 spectrophotometer with an integrated sphere (ILN-472).

3. Results and Discussion

Monomers **5a**–**5e** were all polymerizable in the solid state by UV irradiation. Introduction of a urethane group for intermolecular hydrogen bonding increases probability of

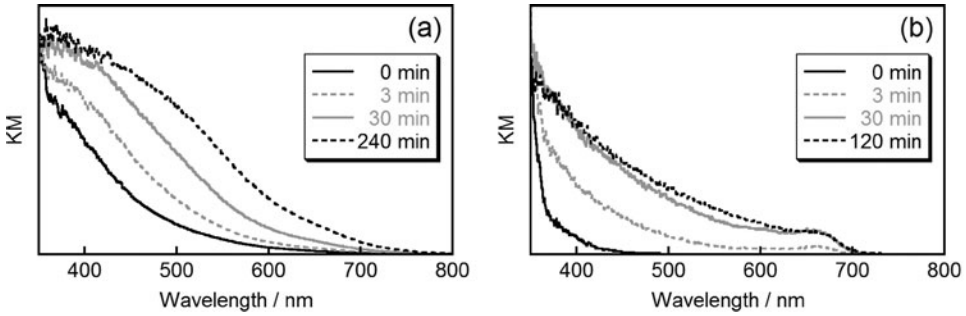

Figure 2. Change in UV-visible diffuse reflectance spectra of **5a** and **5e** depending on irradiation time of UV at 254 nm.

solid-state polymerization [5, 6]. Figure 2(a) shows the diffuse reflectance spectral change of **5a** during photopolymerization as a typical example. Absorption increase in the visible region indicates formation of π-conjugated backbones. However, the excitonic absorption band, which was observed for 27-[4-(dimethylamino)phenyl]heptacosa-24, 26-diynoic acid at about 680 nm [7], was unclear except **5e**, and the backbone structure seemed to be distorted. Only for **5e**, a weak excitonic peak appeared at around 660 nm as shown in Fig. 2(b). Conversion of **5a**, **5b**, **5c**, **5d** and **5e** was obtained to be 11%, 9%, 4%, 9% and 17%, respectively. On the other hand, photopolymerization of **6** was not observed.

CT complex formation of **5a** was confirmed by satisfying the following conditions: (i) Color darkening due to appearance of the CT bands and (ii) no change in NMR spectra, i.e., spectra assigned to be summation of the original components after mixing indicates no new covalent bonds due to the reaction. Since it has been reported that [4-(dimethylamino)phenyl]acetylene derivatives reacted with tetracyanoethylene (TCNE) or TCNQ through [2 + 2] cycloaddition and the following ring opening [8, 9], other acceptors such as 1,4-benzoquinone (BQ), chloranil, 2,4,7-trinitrofluorenone (TNF) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were combined. In the solution mixing method, TNF and DDQ showed color change of the mixed solution. Diffuse reflectance spectra after solvent evaporation of the mixture of **5a** with TNF or DDQ are shown in Figs. 3(a) and (b). Although both of them showed broad absorption in visible region, the CT sites were different. From the NMR study, DDQ was found to give a [2 + 2] adduct with **5a**, i.e., a C≡C bond next to the 4-(dimethylamino)phenyl group of the butadiyne monomers and a C=C bond substituted by two cyano groups in DDQ reacted to form a cyclobutene ring. Similar [2 + 2] cycloaddition reaction between acetylene and DDQ has been recently reported [10]. Thus, the broad visible absorption for the mixture of **5a** and DDQ was concluded to be intramolecular CT in the adduct. On the other hand, condition (ii) was satisfied for TNF. Namely, the CT complex formation was confirmed for the mixture of **5a** and TNF, and the broad visible absorption was assigned to intermolecular CT. Reaction of TNF with the donor monomers seems to be unfavorable because aromaticity of the compounds will be lost after the reaction like the case of DDQ. For weaker acceptors of BQ and chloranil, clear color change of the mixed solution was not observed. However, by powder co-grinding, in which effective concentration of the components increased, both of BQ and chloranil showed color change due to CT-complex formation with **5a**. Diffuse reflectance spectra of these CT complexes are displayed in Figs. 3(c) and (d). For the reference compound **6**, the same behaviors toward acceptors as **5a** were observed. Namely, the 1:1 adduct via [2 + 2] cycloaddition was isolated for DDQ, and other acceptors afforded CT complexes by the

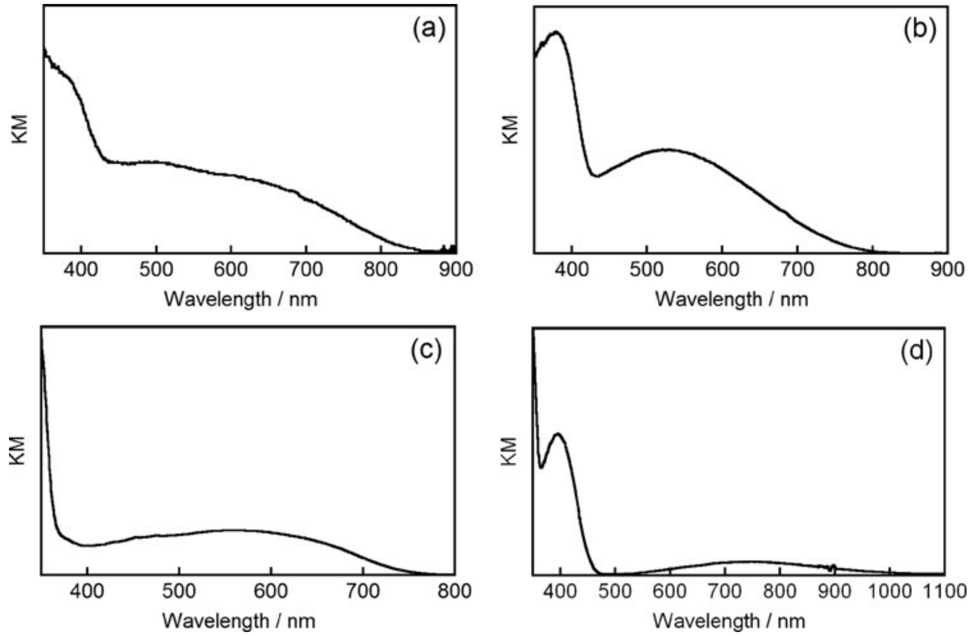

Figure 3. UV-visible-NIR diffuse reflectance spectra of the mixtures of **5a** with (a) TNF, (b) DDQ, (c) BQ and (d) chloranil. Preparation conditions of the mixtures are described in the text.

same method used for **5a**. Thus, we found three types of donor-acceptor interactions between 4-(dimethylamino)phenylbutadiyne derivatives and acceptors, i.e., adduct formation, CT-complex formation even in the mixed solution and CT-complex formation by mixing in the solid state.

4. Conclusion

A series of 4-(dimethylamino)phenylbutadiyne derivatives **5a**–**5e** and **6** were synthesized, and **5a**–**5e** were found to be photopolymerizable in the solid state. Since these monomers are good donors, CT-complex formability of **5a** and **6** with some acceptors was investigated. DDQ gave the [2 + 2] adducts while TNF formed the CT complexes in the mixed solution. Although BQ and chloranil did not form the CT complexes in the mixed solution, they could be prepared by powder co-grinding. Further studies on structures and properties, including solid-state polymerizability and conductivity, of the CT complexes are in progress.

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