Diacetylene-containing polymers XII. Synthesis and characterization of dye-containing poly(hexa-2,4-butadiynylenoxydibenzoates)

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Abstract—Several novel diacetylene-containing polymers containing diacetylenic groups in the main chains and dyes in the side-chains were synthesized using *para-* and *meta-*propargyloxybenzoic acids and four azo dyes. The polymers were synthesized by the oxidative coupling polymerization of dye-containing bisacetylenic monomers, and were characterized and their thermal properties examined. All of the polymers gave thin films with excellent optical quality by casting or spin coating. They showed T_g at around 100°C and the diacetylenic groups cross-linked on heating at above 160°C. The UV-irradiated spin-coated films were no longer soluble in the solvent and did not even swell or come off from the substrate, indicating that the films cross-linked completely.

*Keywords*: Diacetylene; cross-linking; polar dyes; second order NLO.

1. INTRODUCTION

There are a great number of papers reporting polymeric materials which contain highly polar dye molecules, prepared with the objective of obtaining organic materials for applications in second-order nonlinear optics (NLO) [1–3]. Many of these materials consist of vinyl polymer main chains, for example, poly(methyl methacrylate), to which dyes (chromophores) such as 4-{4-[(*N*,*N*-ethyl 2-hydroxyethyl)amino]phenylazo}nitro-benzene (Disperse Red 1) are linked, and their NLO properties and applications have been intensively investigated [4–6]. In addition to the vinyl polymer systems, other types such as polyamides and imides have also been synthesized and their second-order optical nonlinearity has been investigated [7, 8].

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For applications in second-order NLO, these polymers are subjected to orientate their chromophores (dye molecules) in such a manner that there is no centrosymmetry; this is usually achieved by poling the polymer films at temperatures above their glass transition temperatures. However, the orientated chromophores invariably tend to return to their random state and this relaxation on standing diminishes the NLO effect. It is well known that the relaxation could be avoided or considerably slowed if the polymers have high glass transition temperatures or if they are cross-linked; many studies on this subject can be found in the literature. However, polymers having high glass transition temperatures have the disadvantage of being difficult to pole and the orientation of the chromophore groups is less effective.

This paper deals with the synthesis of novel polymers containing azo chromophores and a diacetylenic group, which can be used for cross-linking during the poling process; their cross-linking behavior is also described. Dalton and coworkers have previously reported a polymer containing diacetylene and an azo dye of the following structure [9]:
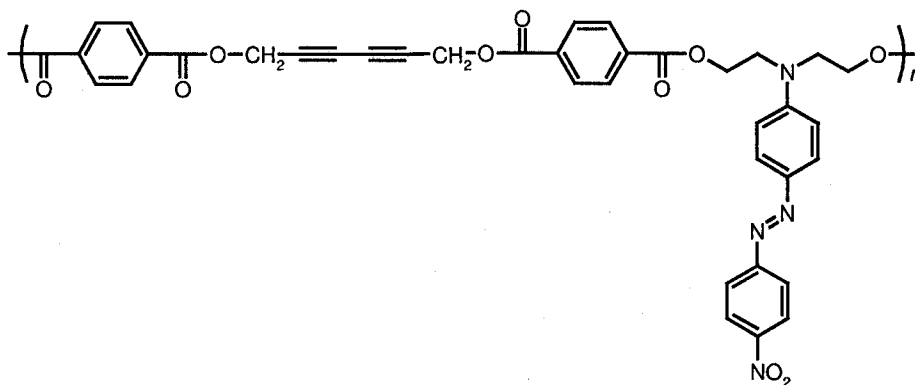

The polymers of this work differ from the above polymer in that they have an ether linkage between the benzoate and propargyl groups, instead of the ester linkage; it is thought that the ether linkage will facilitate the orientation by poling of chromophore groups due to its flexibility, which is one of the most important factors for high second-order NLO susceptibility. High chromophore concentrations of these polymers are expected to exhibit high susceptibility.

2. EXPERIMENTAL

2.1. Monomer synthesis

2.1.1. Acetylenic monomers.   4-Hydroxybenzoic acid (Aldrich) was dissolved in methanol and the required amount of sodium hydroxide was added at room temperature. Then a 10% excess of propargyl bromide (Aldrich) was added to the solution and the mixture was stirred at room temperature, monitoring the reaction by thin layer chromatography. After the reaction, the product was added to water and the system was acidified with hydrochloric acid. The precipitate was filtered,

washed with water, and dried in vacuum. *p*-Propargyloxy-benzoic acid (**1**) was obtained with 70% yield. Recrystallization from n-butanol gave colorless crystals with mp 210–212°C. IR (cm^{-1}) (KBr): 3270 ($\equiv$C$-$H), 3150–3100 (COO$-$H), 2970 (CH$_2$), 2120 (C$\equiv$C), 1690 (C$=$O), 1600 (C$=$C$_{arom}$). ^{1}H-NMR (200 MHz, DMSO-d$_6$): δ (ppm) = 3.61 (s, 1H, H^1), 4.87 (s, 2H, H^3), 7.04 (d, 2H, J = 8.7 Hz, H^5), 7.79 (d, 2H, J = 8.7 Hz, H^6). ^{13}C-NMR: δ (ppm) = 55.66 (C^3), 65 (C^2), 114.53 (C^5), 123.74 (C^7), 131.24 (C^6), 160.7 (C^4), 166.88 (C^8). The signal of C^1 was covered with that of the solvent.
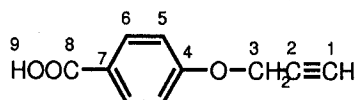

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m-Propargyloxy-benzoic acid was prepared by the same method as that used for the *para* acid.

The acid thus obtained was reacted with thionyl chloride (1.3 mol equivalent to the acid) in dichloromethane at room temperature, using a few drops of dimethylformamide as an accelerator to obtain 4-propargyloxybenzoyl chloride. After evaporating the solvent and the excess thionyl chloride under vacuum, a hard brown solid melting at 35°C was obtained; this was used for the next step without further purification. IR (cm^{-1}); 1785 (Cl$-$C$=$O).

2.1.2. Synthesis of chromophores. These azobenzene-type chromophores were prepared by the diazonium coupling reaction of 4-nitroaniline or 4-cyanoaniline with *N,N*-bis-2-hydroxyethylaniline. 6.2 g (0.045 mol) of 4-nitroaniline was dissolved in 50 ml of water containing 11.3 ml of concentrated hydrochloric acid and the solution was cooled to 0°C. Then 3.1 g (0.045 mol) of sodium nitrate dissolved in a minimum quantity of water was added dropwise and the mixture was stirred for 20 min. This solution of diazonium salt was then added gradually (0.5 ml each time) to a slightly acidic aqueous solution containing 8.14 g (0.045 mol) of *N,N*-bis-2-hydroxyethylaniline and the mixture was stirred at room temperature for 8 h. Addition of sodium bicarbonate to neutralize the solution precipitated the product, which was filtered and dried. The chromophore **2** was recrystallized from a n-butanol–toluene mixture (80 : 20, vol.) or from acetonitrile (mp 201–203°C). Yield: 83% (12.4 g). IR (cm^{-1}) (KBr): 3271 (O$-$H), 2880 (CH$_2$), 1600 (C$=$C$_{arom}$). ^{1}H-NMR (DMSO-d): δ (ppm) = 3.6 (s, 4H, H^1, H^2), 4.89 (s, 1H, H^{11}), 6.9 (d, 1H, J = 8.7 Hz, H^4), 7.81 (d, 1H, J = 9.3 Hz, H^5), 7.92 (d, 1H, J = 9.0 Hz, H^8). ^{13}C-NMR: δ (ppm) = 53.35 (C^2), 58.16 (C^1), 111.67 (C^4), 122.43 (C^5), 124.97 (C^8), 126.03 (C^9), 142.64 (C^6), 146.73 (C^{10}), 152.33 (C^3), 156.27 (C^7). This compound is now available commercially.
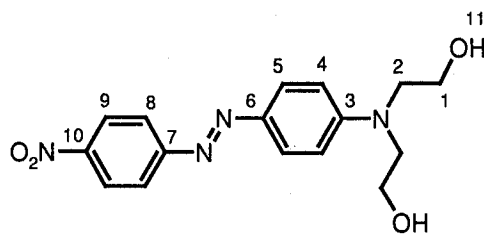
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Similarly to the above-mentioned method, the chromophore **3** was synthesized using 6 g (0.05 mol) of 4-cyanoaniline. The product was recrystallized from toluene (mp 167–168°C), and the yield was 76% (11.9 g). IR (cm^{-1}) (KBr): 3420 (O–H), 2881 (CH$_2$), 2220 (C≡N), 1595 (C=C$_{arom}$). ^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) = 3.59 (s, 4H, H^1, H^2), 6.88 (d, 1H, J = 8.7 Hz, H^4), 7.79 (d, 1H, J = 9.3 Hz, H^5), 7.95 (d, 1H, J = 9.0 Hz, H^8). ^{13}C-NMR: δ (ppm) = 58.33 (C^2), 53.29 (C^1), 118.79 (C^{11}), 161.55 (C^4), 122.33 (C^5), 125.72 (C^8), 133.52 (C^9), 142.42 (C^6), 133.52 (C^{10}), 152.05 (C^3), 154.89 (C^7).
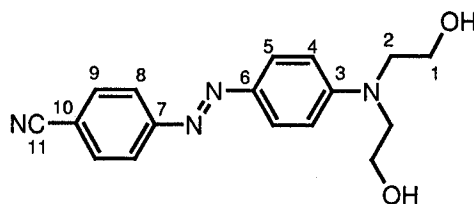

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Chromophores of the diazobenzene type required two diazotizations. 4.13 g (0.035 mol) of 4-cyanoaniline was converted to the diazonium salt as in the above case, and was reacted with 4.24 g (0.035 mol) of 3,5-dimethylaniline to obtain the compound **4**, which was isolated and recrystallized from toluene. Crystals melting at 141–142°C were obtained with 85% yield. IR (cm^{-1}): 3450 and 3370 (N–H), 2916 (–CH$_3$), 1596 (C=C$_{arom}$), 2223 (–C≡N). ^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) = 2.5 (s, 3H, H^{10}), 4.0 (s, 1H, H^{11}), 6.4 (s, 1H, H^2), 7.7 (d, 1H, J = 5.4 Hz, H^7), 7.8 (d, 1H, J = 5, 4 Hz, H^6). ^{13}C-NMR: δ (ppm) = 21.15 (C^{10}), 112.02 (C^8), 118.89 (C^9), 122.49 (C^6), 133.03 (C^7), 137.88 (C^3), 142.09 (C^4), 148.98 (C^1), 155.82 (C^5).
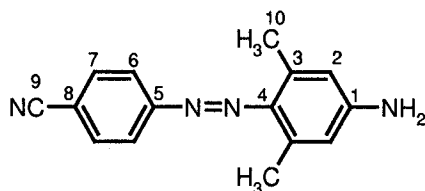

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7 g (0.028 mol) of compound **4** were converted to the diazonium salt by the same method described previously and was coupled with 5.1 g (0.028 mol) of *N*,*N*-bis-2-hydroxyethylaniline to obtain **5**. The resulting chromophore was recrystallized

from ethyl acetate and crystals melting at 203–205°C were obtained with 62% (9 g) yield. IR (cm^{-1}) (KBr): 3222 (O–H), 2928 (CH_3, CH_2), 2222 ($C\equiv N$), 1597 ($C=C_{arom}$). ^{1}H-NMR (200 MHz, acetone-d): δ (ppm) = 3.82 (q, 2H, H^1), 3.73 (q, 2H, H^2), 4.89 (s, 1H, H^{11}), 6.93 (d, 1H, J = 9.3 Hz, H^4), 7.66 (s, 1H, H^8), 7.85 (d, 1H, J = 9.3 Hz, H^5), 8.06 (d, 2H, J = 8.8 Hz, H^5, H^{12}). ^{13}C-NMR: δ (ppm) = 20.0 (C^{16}), 55.0 (C^2), 60.1 (C^1), 112.6 (C^4), 114.4 (C^{14}), 119.7 (C^{15}), 123.9 (C^5, C^{12}), 126.1 (C^8), 134.4 (C^6, C^9), 151.5 (C^3), 152.1 (C^7), 125.72 (C^8), 133.52 (C^{10}), 152.05 (C^3), 154.0 (C^{10}), 156.0 (C^{11}).
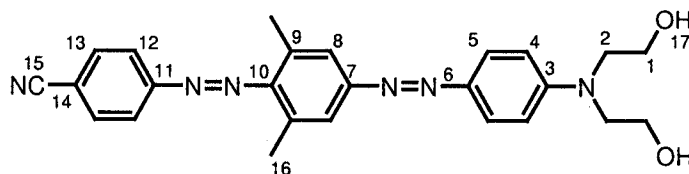

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Similarly to the above, the nitro derivative **6** was obtained as a dark red solid melting at 114–115°C, with a total yield of 72%.
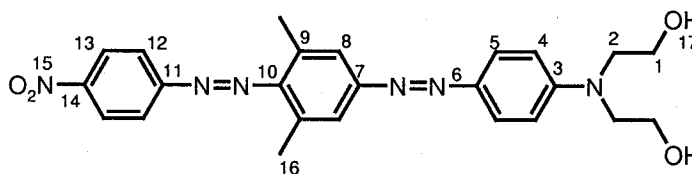

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2.1.3. Synthesis of bisacetylenic monomers.

2.1.3.1. 4-N,N-bis[2-(propargyloxybenzoyloxyethyl)-amino]-4'-nitroazobenzene (7). 5 g (0.015 mol) of chromophore **2** was reacted at room temperature with 6.43 g (0.033 mol) of the acid chloride in dry dichloromethane, using dry triethylamine as an acid acceptor. The reaction was monitored by thin layer chromatography. Dichloromethane and the excess triethylamine were then evaporated under vacuum and triethylamine hydrochloride was washed off with water. The products were dried and recrystallized repeatedly from toluene. An intense red crystalline solid melting at 145–146°C was obtained with 66% yield. Elemental analysis (%). Found: C, 66.61; H, 4.66; N, 8.37. Calc. for $C_{36}H_{30}N_4O_8$: C, 66.87; H, 4.64; N, 8.66. IR (cm^{-1}) (KBr): 3272 ($\equiv C–H$), 3060 ($=C–H_{arom}$), 2922 (CH_2), 2129 ($C\equiv C$), 1688 ($OC=O$), 1604 ($C=C_{arom}$). ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ (ppm) = 3.6 (s, 1H, H^1), 3.9 (t, 2H, H^8), 4.6 (t, 2H, H^9), 4.8 (d, 2H, J = 2.1 Hz, H^3), 7.0 (d, 2H, J = 9.0 Hz, H^5), 7.1 (d, 2H, J = 9.3 Hz, H^{11}), 7.85 (d, 2H, J = 9.3 Hz, H^{12}), 7.89 (d, 2H, J = 8.7 Hz, H^{15}), 7.95 (d, 3H, J = 9.0 Hz, H^6, H^{16}). ^{13}C-NMR: δ (ppm) = 49.03 (C^3), 55.68 (C^9), 61.9 (C^8), 78.95 (C^1), 79.38 (C^2), 112.22 (C^{11}), 114.77 (C^5), 122.26 (C^7), 122.61 (C^{12}), 124.95 (C^{15}), 125.84 (C^{16}), 131.25 (C^6), 143.42 (C^{13}), 147.04 (C^{17}), 151.87 (C^{10}), 156.07 (C^{14}), 161.07 (C^4), 165.31 (C^{18}).
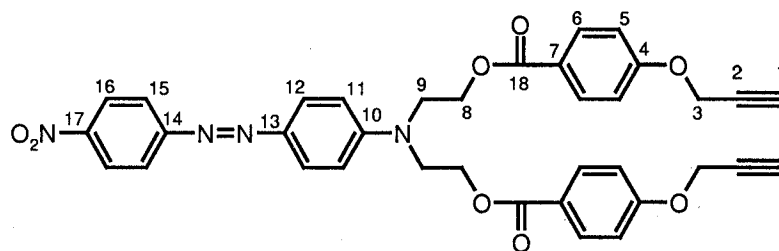
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2.1.3.2. Synthesis of 4-N,N-bis[2-(p-propargyloxybenzoyloxyethyl)-amino]-4'-cyanoazobenzene (8). The monomer was obtained by reactions of the dialcohol **3** with p-propargyloxybenzoyl chloride [5 g (0.016 mol) of chromophore **3** with 2.2 equivalents (0.035 mol) of the acid chlorides]. The product monomers were recrystallized two or three times from a mixture of toluene and hexane. Orange crystals melting at 85–87°C were obtained with 66% yield. Elemental analysis: Calcd. for C_{37} $H_{30}N_4O_6$: C, 70.92; H, 4.79; N, 8.94%. Found: C, 71.3; H, 4.74; N, 8.91%. IR (cm^{-1}) (KBr): 3259 $(\equiv C-H)$, 3064 $(=C-H_{arom})$, 2890 (CH_2), 2225 $(C\equiv N)$, 2117 $(C\equiv C)$, 1687 $(OC=O)$, 1604 $(C=C_{arom})$. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.6 (s, 1H, H^1), 3.9 (t, 2H, H^9), 4.5 (t, 2H, H^8), 4.7 (s, 2H, H^3), 6.9 (d, 3H, J = 8.9 Hz, H^5, H^{11}), 7.7 (d, 1H, J = 8.7 Hz, H^{16}), 7.91 and 7.97 (d, 4H, J = 9.4 Hz, H^{12}, H^6, H^{15}). ^{13}C-NMR: δ (ppm) = 49.93 (C^9), 55.88 (C^3), 61.56 (C^8), 76.18 (C^1, C^2), 111.98 (C^{11}), 114.66 (C^5), 118.9 (C^{17}), 122.85 (C^7, C^{18}), 126.0 (C^{12}, C^{15}), 131.69 (C^6), 133.10 (C^{16}), 144.32 (C^{13}), 150.47 (C^{10}), 155.31 (C^{14}), 161.47 (C^4), 165.93 (C^{19}).
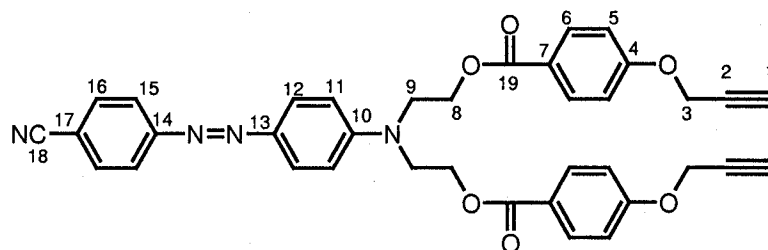

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2.1.3.3. Synthesis of 4-N,N-bis[2-(m-propargyloxybenzoyloxyethyl)amino]-4'-cyanoazobenzene (9). This monomer was synthesized by the same method as that used for the synthesis of **8**, except that m-propargyloxybenzoyl chloride was used. The chloride was prepared by the chlorination of m-propargyloxybenzoic acid with thionyl chloride. The monomer was recrystallized from methanol and orange crystals melting at 94°C were obtained, with an overall yield of 85%. IR (cm^{-1}) (KBr): 3276 $(\equiv C-H)$, 2960 $(-CH_2-)$, 2219 $(-C\equiv N)$, 2117 $(C\equiv C)$, 1718 $(O-CO-)$, 1596 $(C=C_{arom})$. ^{1}H-NMR (acetone-d): δ (ppm) = 3.08 (s, 1H, H^1), 4.15 (t, 2H, H^{11}), 4.65 (t, 2H, H^{10}), 4.82 (s, 2H, H^2), 7.2 (d, 2H, H^{13}), 7.25 (dd, J = 0.9 and 2.7 Hz, 2H, H^5), 7.42 (t, 2H, H^8), 7.62 (m, 4H, H^9, H^{14}), 7.9 (m, 6H, H^7, H^{17}, H^{18}).

^{13}C-NMR: 50.4 (C^{11}), 56.67 (C^{10}), 63.23 (C^3), 77.48 (C^1), 79.47 (C^2), 113.23 (C^{13}), 116.26 (C^5, C^{19}), 119.39 (C^{20}), 121.15 (C^7, C^9), 123.48 (C^{14}), 126.75 (C^8), 130.65 (C^6), 134.25 (C^{18}), 144.92 (C^{15}), 152.8 (C^{12}), 156.35 (C^{16}), 158.77 (C^4), 166.65 (C^{21}).
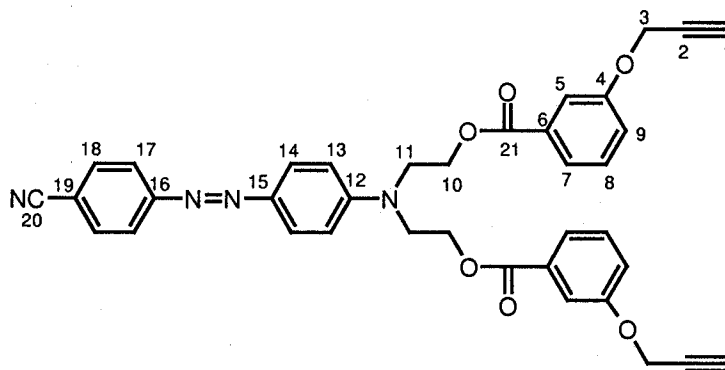

9

2.1.3.4. Synthesis of 4-N,N-bis[2-(4-propargyloxybenzoyloxy)ethylamino]-3',5'-dimethyl-4'-(4''-nitrophenylazo)-azobenzene (10). This monomer was prepared by the above-mentioned method using 4.6 g (0.01 mol) of **6** with 5 g (0.026 mol) of *p*-propargyloxybenzoyl chloride at room temperature, using triethylamine as an acid acceptor. The reaction was monitored by thin layer chromatography. After evaporating the dichloromethane and excess triethylamine in vacuum, the product was recrystallized from n-butanol and purple crystals melting at 93–94°C were obtained, with a total yield of 52% (5.6 g). Elemental analysis: Calcd (%): C, 67.86; H, 4.88; N, 10.80. Found: C, 68.3; H, 4.83; N, 9.71. IR (cm^{-1}) (KBr): 3274 ($\equiv$C$-$H), 2980 and 2915 ($-$CH$_2-$, CH$_3$), 2130 (C$\equiv$C), 1708 ($-$O$-$CO$-$), 1604 (C=C$_{arom}$), 1508 and 1330 (C$-$N). ^{1}H-NMR: δ (ppm) = 2.60 (s, 3H, H^{22}), 3.60 (s, 1H, H^1), 4.14 (t, 2H, H^9), 4.63 (t, 2H, H^8), 4.96 (s, 2H, H^3), 7.15 (d, J = 9.0 Hz, 2H, H^5), 7.28 (d, 1H, J = 9.0 Hz, H^{11}), 7.71 (s, 1H, H^{15}), 7.93 (d, 1H, J = 9.0 Hz, H^{12}), 8.02 (d, J = 8.7 Hz, 2H, H^6), 8.18 (dd, 1H, J = 8.7, 1.8 Hz, H^{19}), 8.53 (d, J = 9.0 Hz, 1H, H^{20}). ^{13}C-NMR: δ (ppm) = 20.33 (C^{22}), 50.40 (C^9), 56.83 (C^8), 63.05 (C^3), 78.96 (C^1), 79.51 (C^2), 113.28 (C^{11}), 115.79 (C^5), 122.46 (C^7), 124.08 (C^{15}), 124.29 (C^{12}), 126.05 (C^{19}, C^{20}), 132.40 (C^6), 133.68 (C^{16}), 145.11 (C^{13}), 149.98 (C^{21}), 151.37 (C^{10}), 152.51 (C^{14}), 154.04 (C^{18}), 157.18 (C^{17}), 162.38 (C^4), 166.7 (C^{23}).
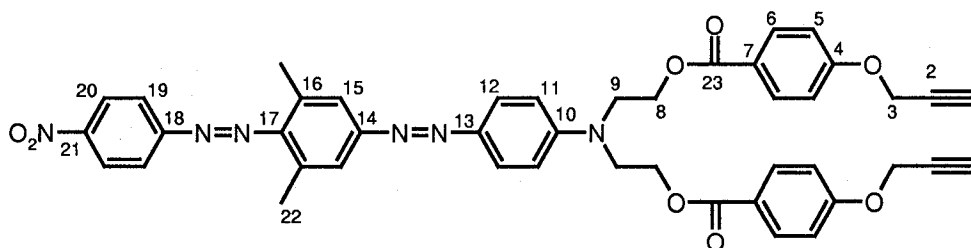

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2.1.3.5. Synthesis of 4-N,N-bis[2-(4-propargyloxybenzoyloxy)ethylamino]-3',5'-dimethyl-4'-(4''-cyanophenylazo)azobenzene (11). By the same method as that above, this monomer was prepared by the reaction of **5** with 4-propargyloxybenzoyl chloride. The product was recrystallized from benzene and purple crystals melting at 94–95°C were obtained, with a total yield of 54%. IR (cm^{-1}) (KBr): 3272 ($\equiv$C$-$H), 3064 (=C$-$H$_{arom}$), 2924 ($-$CH$_2$ and CH$_3$), 2226 (C$\equiv$N), 2129 (C$\equiv$C), 1685 (O$-$C=O), 1604 (C=C$_{arom}$). ^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) = 2.54 (s, 4H, H^1, H^{23}), 3.92 (t, 2H, H^9), 4.55 (t, 2H, H^8), 4.74 (s, 2H, H^3), 6.98 (d, J = 8.9 Hz, 3H, H^5, H^{11}), 7.65 (s, 1H, H^{15}), 7.82 (d, J = 8.9 Hz, 1H, H^{20}), 7.98 (d, J = 8.9 Hz, H^{12}, H^{19}, H^6). ^{13}C-NMR: 19.95 (C^{10}), 49.94 (C^9), 55.89 (C^3), 61.7 (C^8), 76.19 (C^2), 112.01 (C^{11}), 113.95 (C^{21}), 114.67 (C^5), 118.53 (C^{22}), 122.94 (C^7), 123.07 (C^{12}), 123.94 (C^{19}), 125.5 (C^{15}), 131.7 (C^6), 133.31 (C^{20}), 133.79 (C^{16}), 144.02 (C^{13}), 150.36 (C^{10}), 151.85 (C^{14}), 154.85 (C^{18}), 155.89 (C^{17}), 161.46 (C^4), 166.09 (C^{24}). The signal of C^1 was covered by the solvent signal.
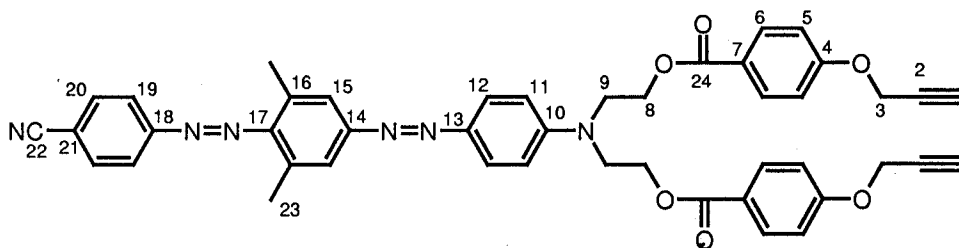

11

2.2. Polymerization

The polymerization was carried out at room temperature in *N*-methyl-2-pyrrolidone using copper(I) chloride and *N,N,N'N'*-tetramethylethylenediamine (TMED), bubbling oxygen in gently while stirring for 4 h with a magnetic bar. The oxidative coupling polymerization proceeds according to the reaction
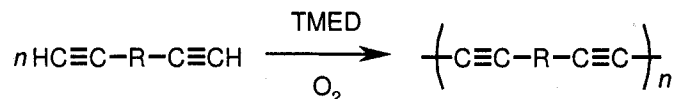
In each polymerization, 2 g of monomer was dissolved in 3–4 ml of *N*-methyl-2-pyrrolidone and 0.02 g of copper(I) chloride, and a few drops of the amine were added. The polymers obtained were precipitated in methanol, washed well with methanol, and dried in vacuum. They were purified by reprecipitation from a chloroform/methanol system. The polymers obtained have the following general structure:
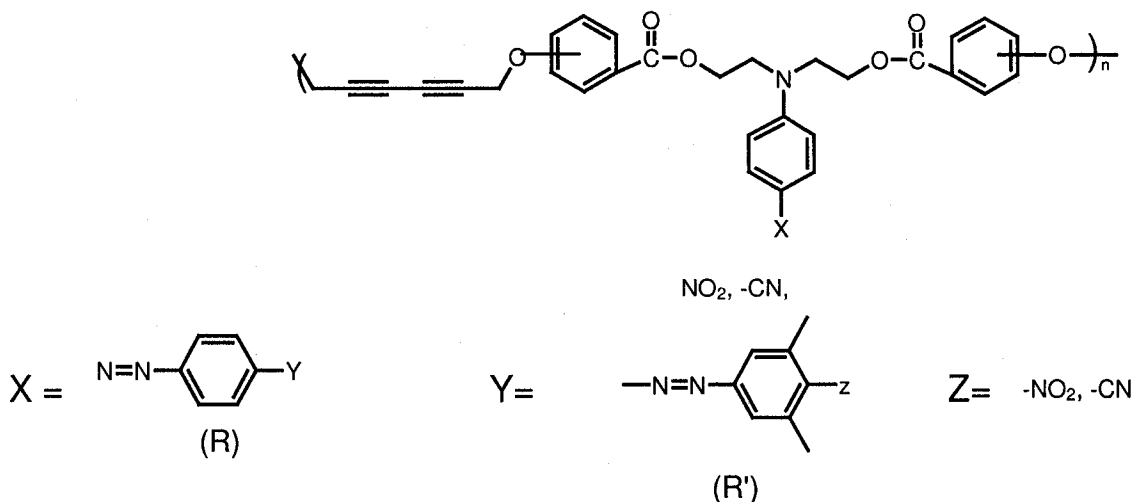
P-7: *para*-benzoate: X = R, Y = $-NO_2$, **P-8**: *para*-benzoate: X = R, Y = $-CN$; **P-9**: *meta*-benzoate: X = R, Y = $-CN$; **P-10**: *para*-benzoate: X = R, Y = R′, Z = $-NO_2$; **P-11**: *para*-benzoate: X = R, Y = R′, Z = $-CN$.

2.3. UV irradiation

An Ace Glass medium pressure mercury lamp (450 W) was used for irradiation of the spin-coated films. The irradiation was performed on a hot plate heated at 120°C for 30–60 min in air at a distance of 25 cm from the lamp.

2.4. Characterization

Elemental analysis was performed by Desert Analytics, Tucson, Arizona. Differential scanning calorimetry (DSC) was carried out using a TA Instrument Calorimeter Model 910. Gel permeation chromatography (GPC) of the polymers was performed in chloroform using a Varian GPC system consisting of a pump (Varian 9002), a column (TSK gel type G4000H8 polystyrene) with a detector (Varian RI-4), and an integrator (Varian 4400). NMR spectra were taken using a Varian 300 MHz (^{1}H) and 75 MHz (^{13}C), and FT-IR spectra were taken using a Nicolet 510p spectrophotometer.

3. RESULTS AND DISCUSSION

The average molecular weights of these polymers determined by GPC using a polystyrene standard were not high, ranging around 1500, but all of them gave films with excellent optical transparency by spin coating from their chloroform solutions. The IR spectra of the polymers did not show a peak at 3237 cm^{-1} due to the remaining terminal acetylenic $\equiv$C$-$H. An example is shown in Fig. 1. The ^{1}H-NMR spectra of the polymers no longer contain the peak of the terminal acetylenic proton, as shown by the example in Fig. 2. The molecular weight of monomer **7**, for
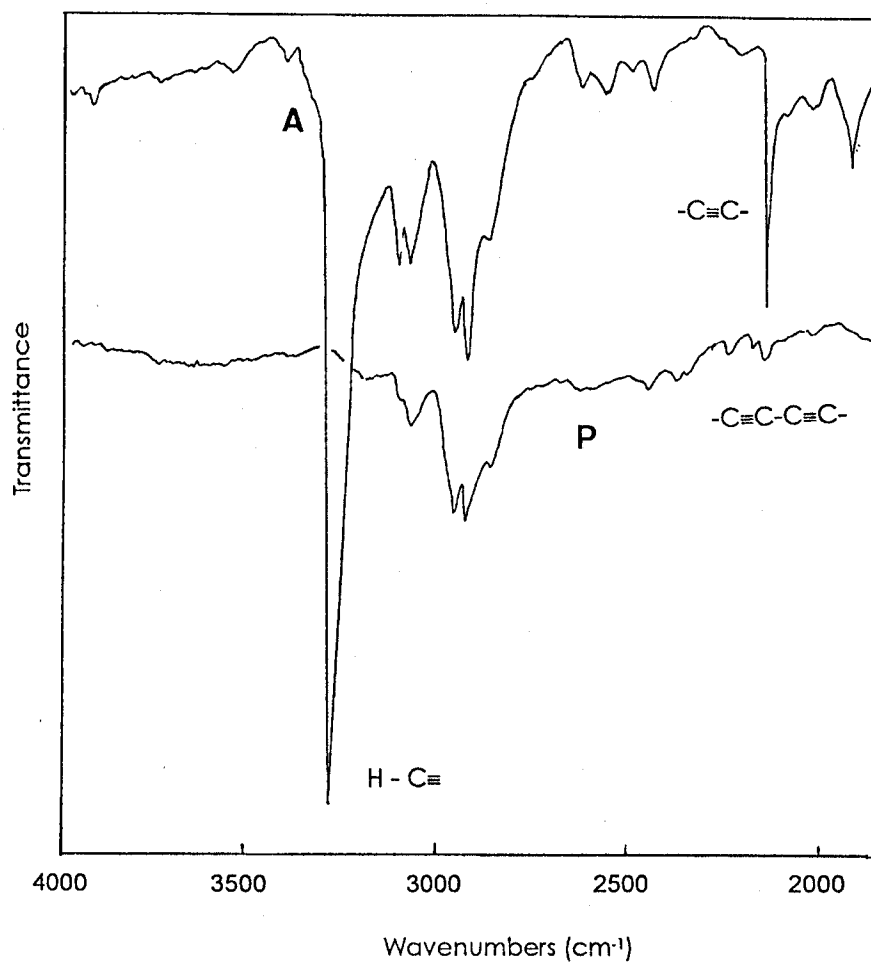
Figure 1. IR spectra of monomer **10** and its polymer **P-10**.
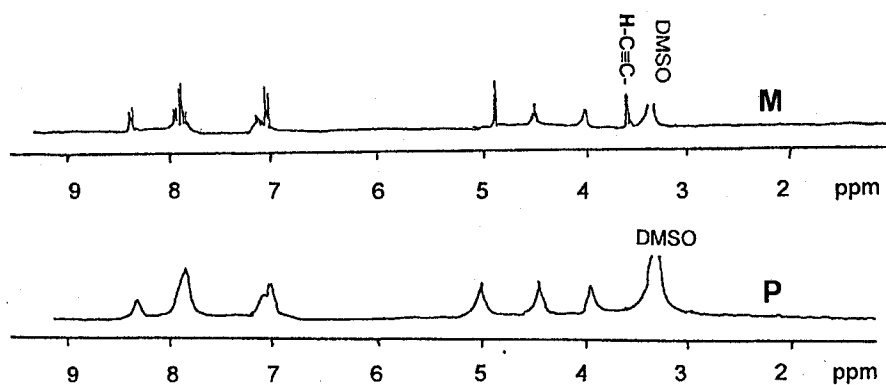

Figure 2. ^{1}H-NMR spectra of monomer **7** and its polymer **P-7**.

example, is 648, and if the polymerization product is an oligomer of molecular weight *ca.* 2000, the IR and NMR spectra should show the terminal acetylenic group. It is thought, therefore, that the unique polymers of this work are simply not adequate for GPC with a polystyrene standard. Therefore, the inherent viscosity of some of these polymers was measured in dimethylacetamide; it was found to be

Table 1.

Thermal behavior of the polymers observed in DSC

Polymer	T_g (°C)	T_{cs} (°C)	T_{cm} (°C)
P-7	106	160	204
P-8	110	150	189
P-9	47	162	180
P-10	130	152	181
P-11	120	150	180

T_g = glass transition temperature; T_{cs} = temperature at which cross-linking starts; T_{cm} = temperature of the exotherm peak due to cross-linking.
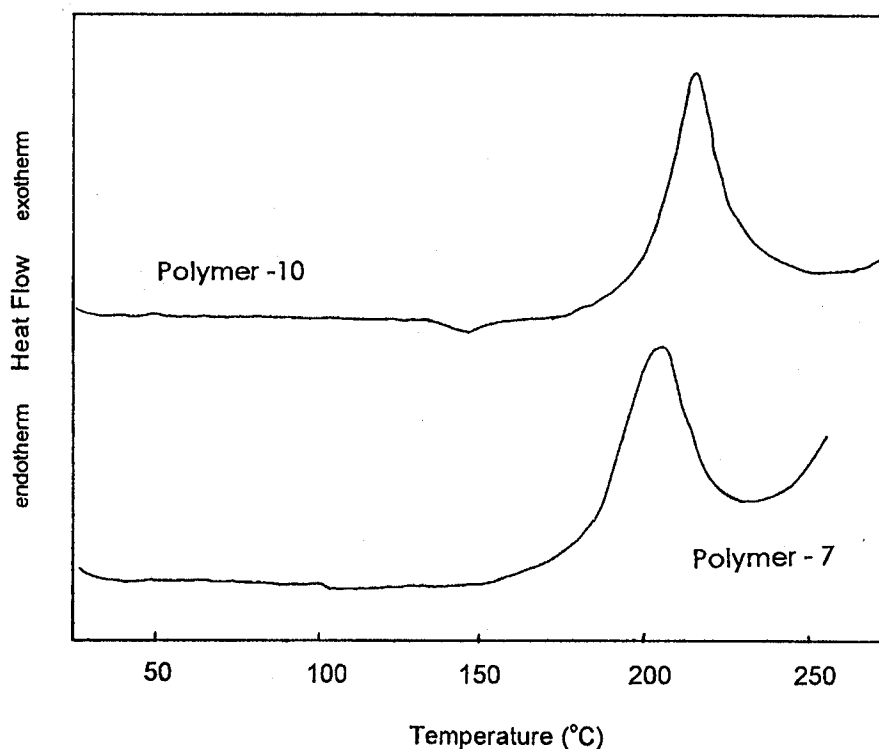

Figure 3. DSC curves of polymers **P-7** and **P-10**. Heating rate = 5°C/min. Under N_2.

of the order of 0.4–0.8 dl/g, showing that these polymers have a medium molecular weight.

In order to examine the thermal behavior of these polymers, DSC was performed; the results are summarized in Table 1 and typical cases are shown in Fig. 3. Cross-linking is important to retard the relaxation of orientated chromophores. The glass transition temperatures, T_g, of these polymers were found to be around 100°C. This T_g range is satisfactory for poling of the chromophores, being neither low nor high. The poling of high T_g polymers, such as polyamides and polyimides, always requires a high temperature, which often decomposes the chromophore group. Thermal cross-linking of the diacetylene groups starts at a temperature of around 160°C and becomes rapid around 180–200°C. Many diacetylene-containing
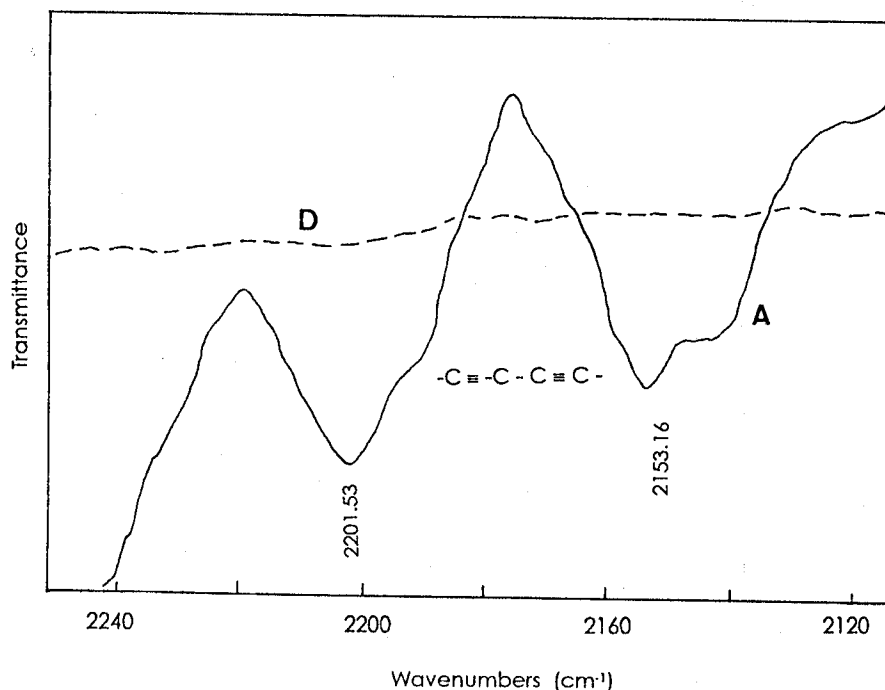
Figure 4. IR spectra of **P-7** before and after heating at 170°C for 30 min.

polymers cross-link rapidly in this temperature range [10, 11]. The diacetylene groups are sensitive to heat and light to form their diradicals, which readily react with each other [12]. Crystalline polymers usually develop a polydiacetylene network, while amorphous ones simply give random cross-linking [13]. At this temperature range, decomposition of the chromophores does not take place and the polymers can be cross-linked. The thermal decomposition was found to initiate at around 230°C by thermal gravimetric analysis. This cross-linking temperature, however, may be too high to maintain the orientation of the poled chromophores during the cross-linking.

The diacetylene groups derived from *p*- and *m*-propargyloxybenzoic acids are not light-sensitive and do not undergo cross-polymerization on standing at room temperature in daylight. However, the spin-coated films irradiated with UV light at 120°C for 1 h became totally insoluble in the solvent chloroform. They did not even peel off from the substrate when soaked in the solvent and did not swell at all, showing that the polymers can be cross-linked efficiently. Figure 4 shows the FT-IR spectra of some of these polymers before and after cross-linking by heat. It can be seen that the typical diacetylene absorption peaks disappeared on heating, indicating that the acetylene groups are used up for cross-linking.

The UV–visible absorption spectra of polymers **P-7** and **P-10** before and after irradiation with UV light at 120°C for 30 min are shown in Figs 5 and 6, respectively. The maxima of these two polymers were the same at 468 nm, despite the different conjugation. The temperature of 120°C was chosen because at this temperature, simultaneous poling and cross-linking are expected to occur. In both cases, some decrease in the intensity and blue shift of the absorption maximum
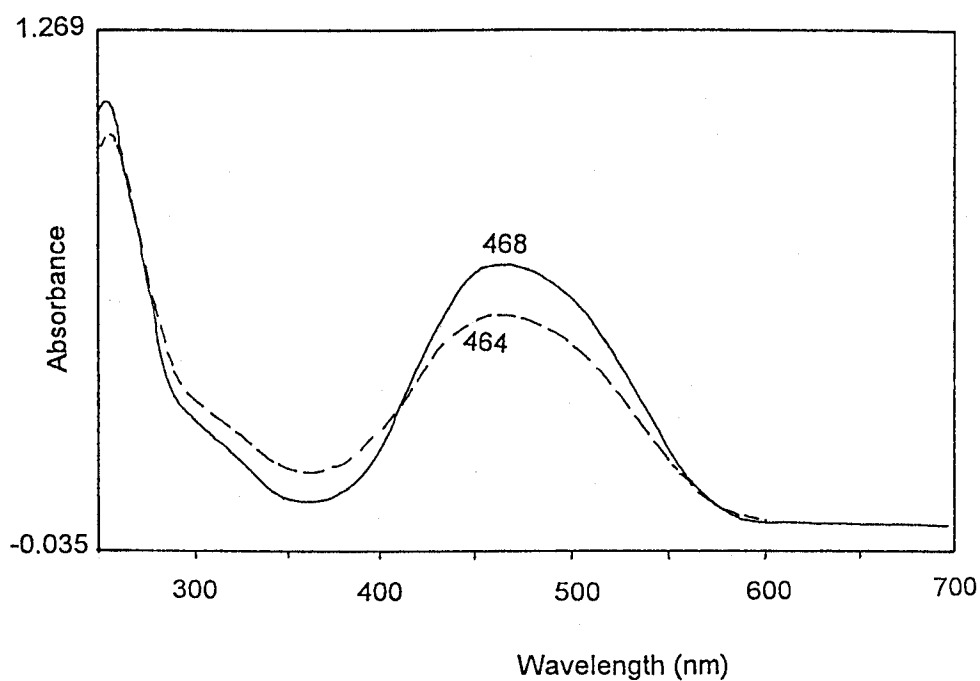
Figure 5. UV–visible spectra of **P-7** before and after irradiation with UV light at 120°C for 30 min.
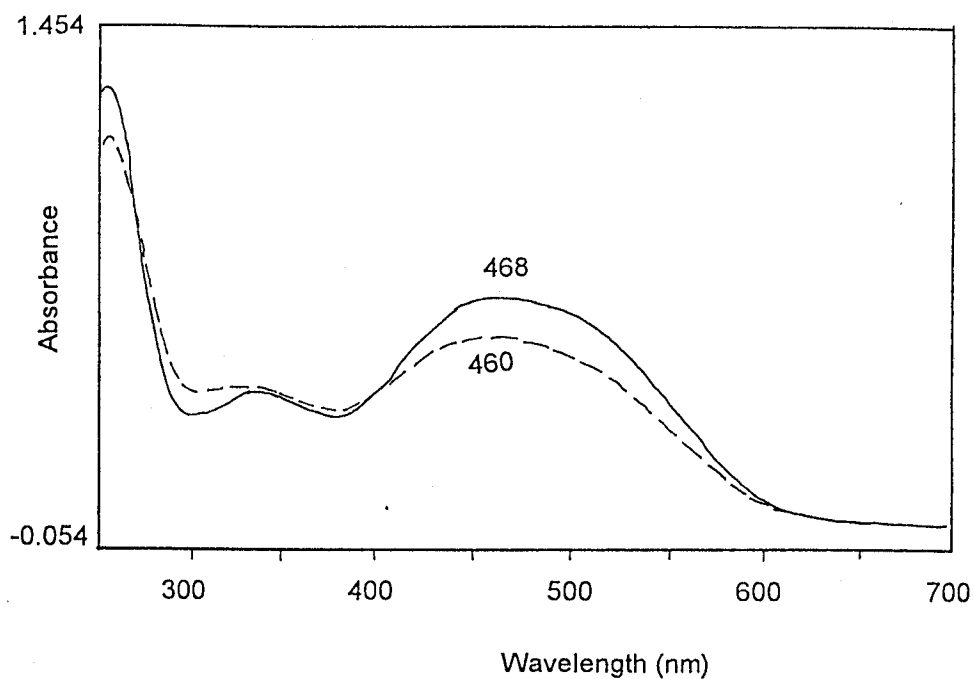

Figure 6. UV–visible spectra of **P-10** before and after irradiation with UV light at 120°C for 30 min.

was observed, due to the *trans–cis* photoisomerization of the azobenzene units. According to the work of Dalton and co-workers [9], the cross-linking by UV irradiation considerably decreased the absorption intensity due to the *cis*-trans isomerization of the azobenzene groups. Such isomerization will differ depending

on the irradiation conditions. There was no appreciable change in the absorption by thermal cross-linking at 170°C.

4. CONCLUSION

Several novel polymers containing diacetylene groups in the main chains and chromophore groups in the side-chains were synthesized, and their thermal and photochemical behavior was studied. It was found that these polymers have very suitable T_g's for poling and that they can be cross-linked to produce thermoset resins. However, a cross-linking temperature of 160°C or more may be too high for simultaneous poling and cross-linking. Cross-linking with UV light is considered to be the best option. These polymers having a high chromophore content and flexible main chains with ether and ester linkages are considered to be ideal polymers for second-order nonlinear optical applications. Studies on their nonlinear optical properties are currently under way and the results will be reported soon.

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