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Studies on diacetylenic vinyl compounds

VII. Synthesis and polymerization of alka-3-5-dinylmethacrylates and 1,8-bis(methacryloxy)octa-3,5-diyne

Lioudmila Fomina, Sergei Fomine, Takeshi Ogawa *

Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico,
Circuito Exterior, Ciudad Universitaria, Apdo. P. 70-360, 04510-México, D.F., Mexico

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Summary

Three alka-3,5-diynylmethacrylate and 1,8-Bis(methacryloxy)octa-3-5-dyine were synthesized and their polymerization in the molten state was studied. 3,5-Octadiynylene-1,8-dimethacrylate, which was the only one that was solid at room temperature, was not light sensitive in the solid state. All the monomers underwent rapid polymerization at 140 °C. The DSC and IR-spectra indicated that the polymerization of the vinyl and diacetylenic groups takes place simultaneously. An optically highly transparent, yellow-orange glass was obtained.

INTRODUCTION

Polydiacetylenes (PDAs) are considered to be promising candidates as materials for nonlinear optical (NLO) applications due to their unique, well defined crystal structures, and many studies on this topic and the values of their third order NLO susceptibilities have been reported in the literature [1,2]. However, the processing of PDAs into optically transparent films is not as easy as that of other polymers, despite the various methods that have been tried. These methods include the preparation of large single crystals [3], Langmuir-Blodgett membranes [4], vacuum evaporation-epitaxy [5], solution casting [6] etc. All these methods have their disadvantages but further improvements are necessary before PDAs are applied in NLO devices. From the processability point of view, DA-containing polymers are interesting materials because they can be processed into thin film by spin coating and the DA groups can be polymerized in the polymer to develop a PDA network in the polymer film [7]. Another method uses a composite film of PDA micricrystals despersed in a transparent film of a common polymer [8]. The third order NLO susceptibility, $\chi^{(3)}$ values of PDA films obtained by the above mentioned methods are around 10^{-9}-10^{-12} esu.

Amorphous-state polymerization of DAs is an interesting topic because extremely transparent and highly conjugated materials can be readily obtained. However not all DAs can be polymerized in the molten state. Some topochemically polymerizing DAs can not be melted because their melting temperatures are higher than the polymerization temperature. The $\chi^{(3)}$ values of the deep red beautifully transparent films obtained by the thermal polymerization of m,m'-butadiynilenedibenzoates have been found to be in the order of 10^{-10} esu [9]. Some DA-containing methacrylates also give red glass when heated or irradiated by γ-rays [10]. In this work, some new aliphatic DA-containing methacrylates and a dimethacrylate were synthesized and their polymerization in the amorphous state was studied.

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* Corresponding author

was dried with Na_2SO_4. Ether was evaporated under vacuum and the residue was distilled under reduced pressure. Yield 75 %. $T_b = 55\text{-}56$ °C/1 mm Hg. FT-IR (cm^{-1}) 3400 (-OH), 2950-2850 (C-H al.), 2220 ($C\equiv CBr$). ^{1}H-NMR (δ) 2.30 (t, 2H $\equiv C\text{-}CH_2\text{-}$), 3.20 (s., 1H HO-), 3.50 (t, 2H O-CH_2).

3-Butynyl methacrylate (3) was prepared by acylation of 3-butyn-1-ol (0.5 mol) by methacryloyl chloride at 0 °C in dioxane solution containing 0.6 mol of triethylamine and purified by distillation in vacuum. Yield 60 %, $T_b = 34\text{-}35$ °C/1mm Hg. IR (cm^{-1}) 3300 ($H\text{-}C\equiv$), 3120 (C-H olef.), 2964-2930 (C-H), aliph), 2124 ($HC\equiv C\text{-}$), 1720 (C=O ester) 1635 (-C=C-). ^{1}H-NMR in $CDCl_3$ (δ) 6.10 (m, 1H, $H_2C=$), 5.72 (m, 1H, $H_2C=$), 4.20 (t, 2H, $\text{-}CH_2\text{-}O\text{-}$), 2.50 (m, 2H, $\text{-}CH_2\text{-}C\equiv$), 2.04 (t, 1H, $HC\equiv$), 1.96 (m, 3H, $CH_3\text{-}$).

Nona-3-5-diyne-1-ol (7), dodeca-3,5-diyne-1-ol (8) and tetradeca-3,5-diyne-1-ol (9): To a solution containing 0.1 mol of terminal acetylene (4, 5 or 6), 25 ml of n-$BuNH_2$, 5 ml of water, 0.1 g of CuCl, 50 ml of MeOH and 2 g of $NH_2OH{\cdot}HCl$, a solution of 4-Bromo-3-butyn-1-ol (2) (0.15 mol) in 200 ml was added dropwise over 3 hrs. at 30-32 °C. Then the solvent was evaporated under reduced pressure the residue was dissolved in CH_2Cl_2 and this solution was washed with diluted HCl and then water. The extract was dried over $MgSO_4$ and CH_2Cl_2 was evaporated under reduced pressure to give the products, each a light yellow oil, with yields of 48, 62 and 53 %, respectively. These compound were analyzed by IR and ^{1}H-NMR spectroscopy and were used in the next step without further purification.

7: IR (cm^{-1}) 3460 (HO-), 2964-2874 (C-H), 2260, 2165 ($\text{-}C\equiv C\text{-}C\equiv C\text{-}$). ^{1}H-NMR in $CDCl_3$ (δ); 4.10 (t, 2H $CH_2\text{-}O\text{-}$), 2.60 (s, 1H, HO-), 2.50 (t, 2H, $\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 2.19 (t, 2H, $CH_3\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 1,50 (m, 2H, $CH_3\text{-}CH_2\text{-}$), 0.90 (t, 3H, CH_3).

8: IR (cm^{-1}) 3450 (HO-), 2960-2870 (C-H), 2260, 2160 ($\text{-}C\equiv C\text{-}C\equiv C\text{-}$) ^{1}H-NMR in $CDCl_3$ (δ); 4.12 (t, 2H $CH_2\text{-}O\text{-}$), 2.55 (s, 1H, HO-), 2.55 (t, 2H, $\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 2.20 (t, 2H, $\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 1.30 (m, 8H, $\text{-}(CH_2)_4\text{-}$), 0.90 (t, 3H, CH3).

9: IR (cm^{-1}) 3450 (HO-), 2965-2875 (C-H), 2260, 2160 ($\text{-}C\equiv C\text{-}C\equiv C\text{-}$) ^{1}H-NMR in $CDCl_3$ (δ); 4.10 (t, 2H $CH_2\text{-}O\text{-}$), 2.39 (s, 1H, HO-), 2.50 (t, 2H, $\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 2.20 (t, 2H, $\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 1.29 (m, 8H, $\text{-}(CH_2)_4\text{-}$), 0.90 (t, 3H, CH_3).

1-(Methacryloyloxy)nona-3,5-diyne (10), 1-(Metacryloyloxy)dodeca-3,5-diyne (11) and 1-(Methacryloyloxy)-tetradeca-3,5-diyne (12): To a solution of compound 10, 11 or 12 (0.12 mol), containing 0.15 mol of triethylamine and 200 ml of THF, methacryloyl chloride (0.18 mol) was added dropwise at 0 °C and the reaction mixture was stirred for 3 hrs at room temperature. The precipitate formed was filtered off, the solvent was evaporated under reduced pressure, the residue was dissolved in hexane and washed with water, dried with $MgSO_4$ and chromatographed on SiO_2 (eluent hexane) to give compounds 10, 11 and 12 as light yellow oils with yields of 70, 82 and 78 %, respectively.

10: IR (cm^{-1}), 3110 (C-H olef.), 2965-2930 (C-H, aliph.), 2260, 2160, ($\text{-}C\equiv C\text{-}C\equiv C\text{-}$), 1723 (C=O ester) 1636 (-C=C-). ^{1}H-NMR in $CDCl_3$ (δ); 5.95 (m, 1H, $H_2C=$), 5.33 (m, 1H, $H_2C=$), 4.15 (t, 2H $CH_2\text{-}O\text{-}$), 2.51 (t, 2H, $\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 2.19 (t, 2H, $CH_3\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 1.89 (m, 3H, $=C(CH_3)$), 1,50 (m, 2H, $CH_3\text{-}CH_2\text{-}$), 0.90 (t, 3H, CH_3).

11: IR (cm^{-1}), 3113 (C-H olef.), 2968-2939 (C-H, aliph.), 2261, 2159, ($\text{-}C\equiv C\text{-}C\equiv C\text{-}$), 1721 (C=0 ester) 1640 (-C=C-). ^{1}H-NMR in $CDCL_3$ (δ); 6.07 (m, 1H, $H_2C=$), 5.46 (m, 1H, $H_2C=$), 4.15 (t, 2H $CH_2\text{-}O\text{-}$), 2.57 (t, 2H, $\text{-}O\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 2.24 (t, 2H, $\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C\equiv$), 1.93 (m, 3H, $=C(CH_3)$), 1,32 (m, 8H, $\text{-}(CH_2)_4\text{-}$), 0.93 (t, 3H, CH_3).

12: IR (cm^{-1}, 3113 (C-H olef.), 2968-2939 (C-H, aliph.), 2261, 2159, ($-C\equiv C-C\equiv C-$), 1721 (C=O ester) 1640 ($-C=C-$). ^{1}H-NMR in $CDCL_3$ (δ); 5.90 (m, 1H, $H_2C=$), 5.40 (m, 1H, $H_2C=$), 4.10 (t, 2H CH_2-O-), 2.50 (t, 2H, $-O-CH_2-CH_2-C\equiv$), 2.19 (t, 2H, $-CH_2-CH_2-CH_2-C\equiv$), 1.91 (m, 3H, $=C(CH_3)$)), 1,29 (m, 8H, $-(CH_2)_6-$), 0.90 (t, 3H, CH_3).

1,8-Bis(methacryloxy)octa-3,5-diyne (13): Through a solution containing 150 ml of 2-propanol, 0.123 mol of 3-butybyl methacrylate (3), 0.1 g of CuCl and 2 ml of N,N,N',N'-tetra-methylenediamine (TMDA), oxygen was bubbled at 60 °C for 48 hrs. Then, the solvent was evaporated under the reduced pressure the solid was washed with dilute hydrochloric acid, and water, dried and crystallized twice from hexane. Yield 48 %, T_m= 59-61 °C. IR (cm^{-1}) 3297 ($H-C\equiv$), 3118 (C-H olef.), 2966-2932 (C-H, aliph.), 2155 ($-C\equiv C-C\equiv C-$), 1725 (C=O ester) 1640($-C=C-$). ^{1}H-NMR in $CDCl_3$ (δ); 6.05 (m, 1H, $H_2C=$), 5.50 (m, 1H, $H_2C=$), 4.15 (t, 2H CH_2-O-), 2.58 (t, 2H, $-O-CH_2-O-$), 2.58 (t, 2H, $-O-CH_2-CH_2-C\equiv$), 1.93 (m, 3H, $=C(CH_3)$)).

The purity of these DAs was also checked by thin layer chromatography (TLC) and elemental analysis. All the monomers gave only one spot in the TLC and their elemental analysis data agree well with their structures.

Polymerization and sample preparation:

The polymerization of the monomers 10, 11, 12 and 13 was carried out under nitrogen. A small amount of the monomer was placed onto a glass, quartz or KBr slide or sandwiched between two slides. The samples were polymerized at 140 °C for 60 min.

Measurements and sample preparation:

DSC was performed at a heating rate of 2 °C/min, under nitrogen with a Dupont 2100. IR-spectra were taken using a Nikolet 510p FT-IR spectrometer in the films on KBr windows. ^{1}H-NMR spectra were taken in $CDCl_3$ solution using a Joel PMX60SI spectrometer. UV-spectra were taken using a UV-260 Shimadzu instrument either, in methanol (monomers) or in the films sandwiched between quartz slides (polymerized products).

RESULTS AND DISCUSSION

All the monomers synthesized were light yellow liquids at room temperature, except 13 which was a solid with a low melting point of 59-61 °C. Therefore, their polymerization in the liquid state was studied. When heated at 140 °C under nitrogen the monomers readily solidified giving glassy, insoluble and transparent orange polymers. It took from 7-10 min for monomer 13 to 60 min for monomer 12 to be solidified. Fig. 1 shows the DSC curves of the monomers. All of them show one exothermic peak around 120-140 °C due to the simultaneous polymerization of both the methacryl and the diacetylenic groups.

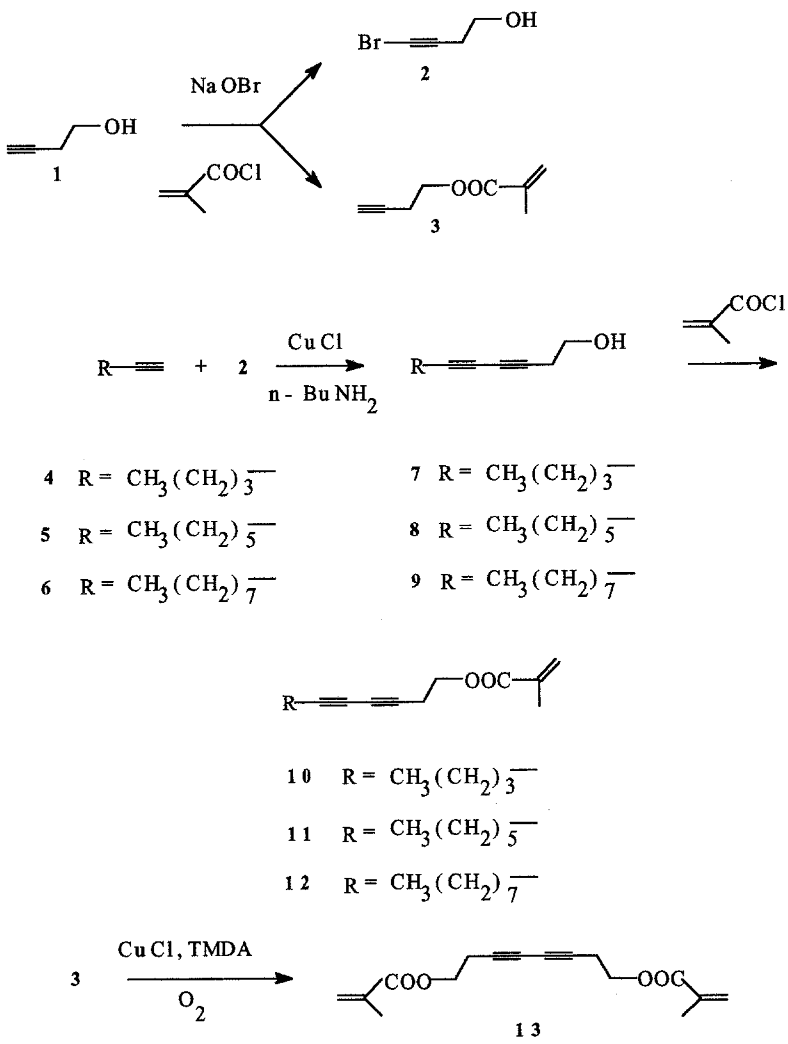
The structure of the polymers formed was studied by FT-IR spectroscopy. Monomers 10, 11, and 12 have two absorption peaks aroun 2260 and 2160 cm^{-1}, corresponding to the symmetrical and unsymmetrical stretching of the diacetylenic groups, respectively. The spectra are very similar to each other in the region of 4000-1400 cm^{-1} and the spectrum of monomer 10 is shown as an example in Fig. 2. Monomer 13 has only one absorption band in the diacetylenic region at 2155 cm^{-1} corresponding to the unsymmetrical stretching of the diacetylenic group. The symmetrical stretching of the diacetylenic groups is not active in the IR spectrum because of the symmetry of the molecule of the monomer 13 (Fig. 2b).

EXPERIMENTAL PART

Materials:

All the reagents were used as received (Aldrich). The synthesis of the monomers is shown in scheme:

Scheme 1



Monomer synthesis:

4- bromo-3-butyn-1-ol (2): To a solution of NaOBr, prepared by mixing a solution of 27 g of NaOH in 100 ml of water and 8 ml of Br_2 at 0 °C, 20 g of 3-butyn-1-ol (1) were added dropwise at 0 °C and the reaction mixture was stirred for 2 hrs at room temperature. Then the mixture was extracted with ether and the extract

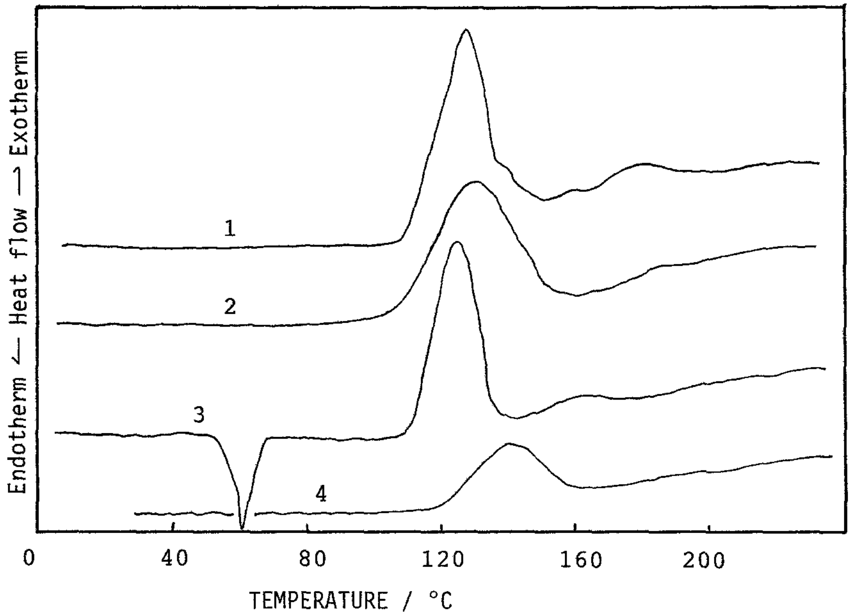
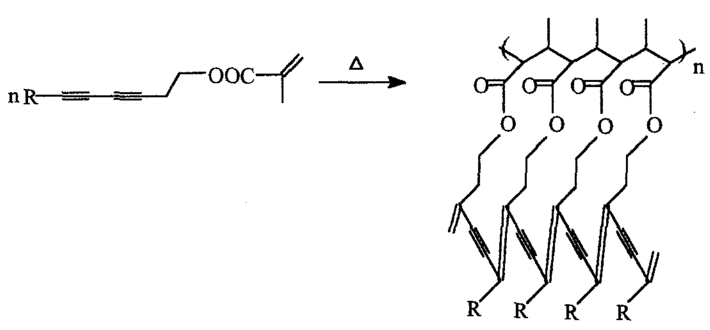


Fig. 1. DSC curves of monomers 10(1), 11(2), 12(3) and 13(4)

When heated at 140 °C for 60 min the IR spectrra of the samples changed drastically. The absorption bands corresponding to the stretching of the diacetylenic groups almost completely disappeared and a new band appeared at 2220 cm^{-1}. An absorption band around 1635-1640 cm^{-1} also disappeared and the carbonyl absorption suffered a hipsochromic shift from 1720 in the monomers to 1740 cm^{-1} in the polymers. These spectral changes indicate the simultaneous polymerization of methacryl and diacetylenic groups. (Scheme 2).

Scheme 2



The disappearance of the diacetylene stretching on polymerization and arising a new band around 2220 cm^{-1} are due to diacetylenic polymerization to form a PDA chain. The peak around 2200 cm^{-1} reflects stretching of the internal -C≡C- bond. FT-IR spectra of **poly-10** and **poly-13** are shown in Fig. 2a and b, respectively, as examples.

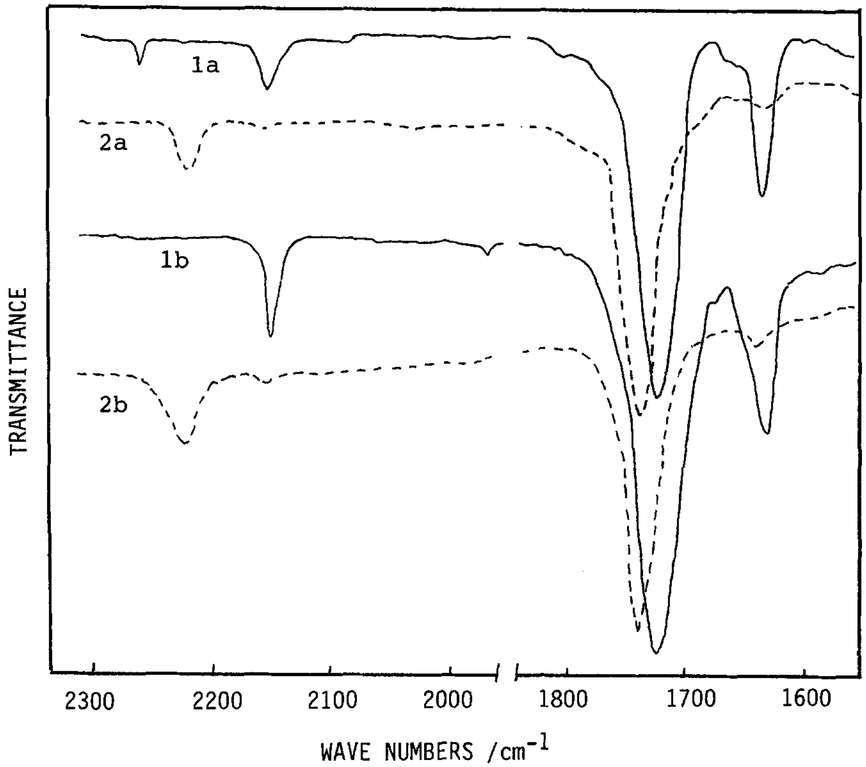


Fig. 2. FT-IR spectra of monomer 10(1a), monomer 13(1b) and their corresponding polymers (2a) and (2b), respectively.

The formation of a conjugated polymer chain is also confirmed by the UV-spectroscopy data. The UV-spectra of all the monomers are similar in appearance. They have no absorptioin beyond 250 nm and have a maximum in the region of 211-216 nm due to the methacryloyl group. The UV-spectra of the polymers are also similar in appearance ans they have no absorption maximum and are characterized by an absorption which starts at 500 nm and which increases towards the shortwave region. This type of UV-spectra is characteristic for amorphous polyconjugated systems. A typical example of the UV-spectra of the UV-spectra of a monomer and polymer is shown in Fig. 3.

It is known that the thermal cross-polymerization of DA-containing polyamides [11], polyesters [12] and some monomeric DAs [13] in the amosphous state give the PDA structure by 1,4-addition, as follows from the FT-IR data: the FT-IR spectra of the DA region of topochemically polymerized samples in the solid state are identical to those of samples polymerized in the amorphous state. This reaction takes place at a temperature of 180-200 °C. In the case of methacrylate-containing DAs the polymerization took place at a lower temperature (exotherm maximum at 120-140 °C). The polymerization of methacryloyl groups facilitates the polymerization of the diacetylene moiety. At first, the polymerization of the methacryloyl groups starts resulting in formation of comb-like or ladder polymers (in the case of monomer **13**) which force the diacetylene groups together thus facilitating their further polymerization.

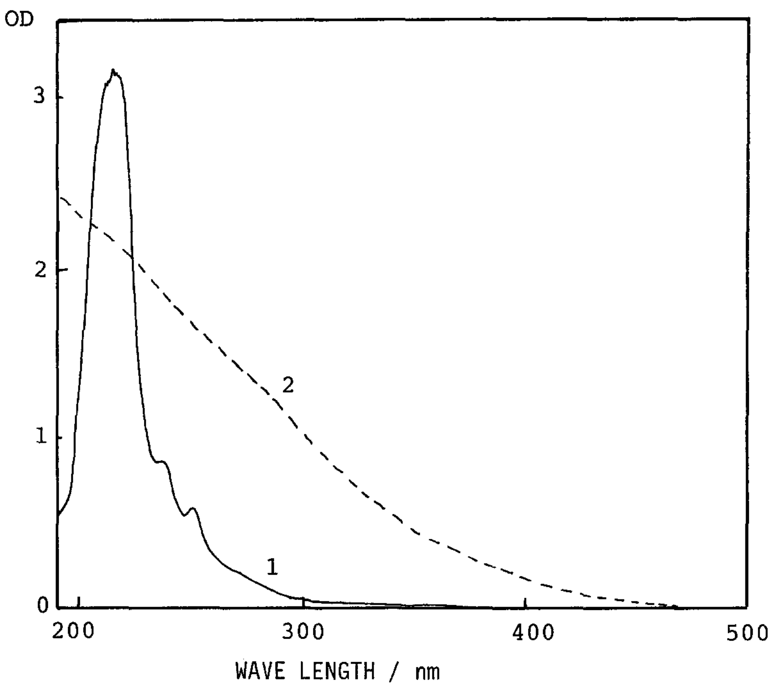


Fig. 3. UV/VIS Spectra of monomer 10 (1) and its polymer(2).

In conclusion, some novel diacetylene-containing acrylates were synthesized and polymerized thermally in bulk to give amorphous transparent insoluble polymers due to simultaneous polymerization of both the methacryloyl and diacetylenic groups.

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