A Study on the Oxidative Coupling Copolymerization of Terminal Bisacetylenes

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Abstract. In order to obtain information on the composition of copolymers formed by the oxidative coupling copolymerization of two different bisacetylenic monomers, oxidative coupling reactions of 5 different pairs of 5 different acetylenes were carried out under the optimum polymerization conditions. The products were isolated quantitatively by extraction and column chromatography, and characterized by FT-IR and NMR spectroscopy. Most of the cases, excellent cross-coupling was observed indicating that random copolymers will be obtained. The photoreactivity of unsymmetric diacetylenes was also determined and the majority of them were photosensitive. Copolymerization of different bisacetylenic aromatic amides with a urethane was also carried out. The copolymers were soluble in *N*-methylpyrrolidone, while the homopolyamides were insoluble.

Resumen. Con el objeto de obtener información sobre la composición de los copolímeros formados mediante el acoplamiento oxidativo de dos diferentes monómeros bisacetilénicos, se llevaron a cabo las reacciones de acoplamiento oxidativo de cinco pares de diferentes acetilenos en condiciones óptimas de polimerización. Los productos resultantes fueron separados cuantitativamente por medio de extracción y cromatografía en columna, caracterizándolos por medio de espectroscopía de FTIR y RMN. En la mayoria de los casos, se observó un excelente acoplamiento cruzado, lo cual sugiere que se podrán obtener copolímeros al azar a partir de los bisacetilenos correspondientes. La mayoría de los diacetilenos obtenidos fueron fotosensibles y desarrollaron color, por efecto de la radiación de electrones acelerados. Se llevó a cabo una serie de copolimerizaciones de amidas aromáticas con un uretano. Los copolímeros resultantes fueron solubles en solventes y sensibles a la radiación.

Key words. Oxidative coupling of acetylenes, diacetylenes, copolymerization, polydiacetylenes.

1 Introduction

Polydiacetylenes (PDAs) are interesting polymeric materials because of their unique conjugation system consisting of double-single-triple-single bonds, and some of them are obtained by the solid state polymerization of the corresponding monomers, as shown in Figure 1. The polymerization, so called "topochemical polymerization"[1] has been investigated by many as it is a unique example that completely crystalline monomers are converted to the corresponding completely crystalline polymers by radiation, pressure or heating at temperatures below their melting points.[2] They have been found to have third order nonlinear optical susceptibility[3] and their optical properties have been extensively investigated by many researchers.[4] However, the majority of PDAs obtained by the solid state polymerization, are poorly soluble in organic solvents and their processing to thin films is rather difficult. There are various methods to obtain thin PDA films, which include Langmuir-Boldgett membrane technique, epitaxial vapor phase deposition, single crystals, etc. These methods however, have some technical dificulties, and new methods which give high optical quality films are being sought. One of them is to prepare processable polymers containing diacetylene (DA) groups in main chains. Figure 2 shows models of DA-containing polymers. They can be readily synthesized either by usual condensation reactions of bifunctional monomers or by the oxidative coupling polymerization, as shown by Figure 3. The DA-containing polymers provide new polymeric materials through chemical reactions of the DA groups. Some light sensitive DA-containing polymers have potential applications as photoresists, radiation and heat sensors, third order nonlinear optical films, etc. Other reactions such as halogenation, and thiophene and pyrrole ring formation, provide various new products of interest. There are many DA-containing polymers and they are listed in a recent review article.[5] The oxidative coupling polymerization also provides a useful method to incorporate functional compounds into polymer chains. For example, fluorescein containing terminal acetylenes can be readily incorporated in polymer main chains.[6]

Very little has been studied on the copolymerization of different bisacetylenic monomers. Copolymerization is an important process in order to modify polymer morphology, thus drastically changing chemical and physical properties of polymers, such as thermal properties, solubili-

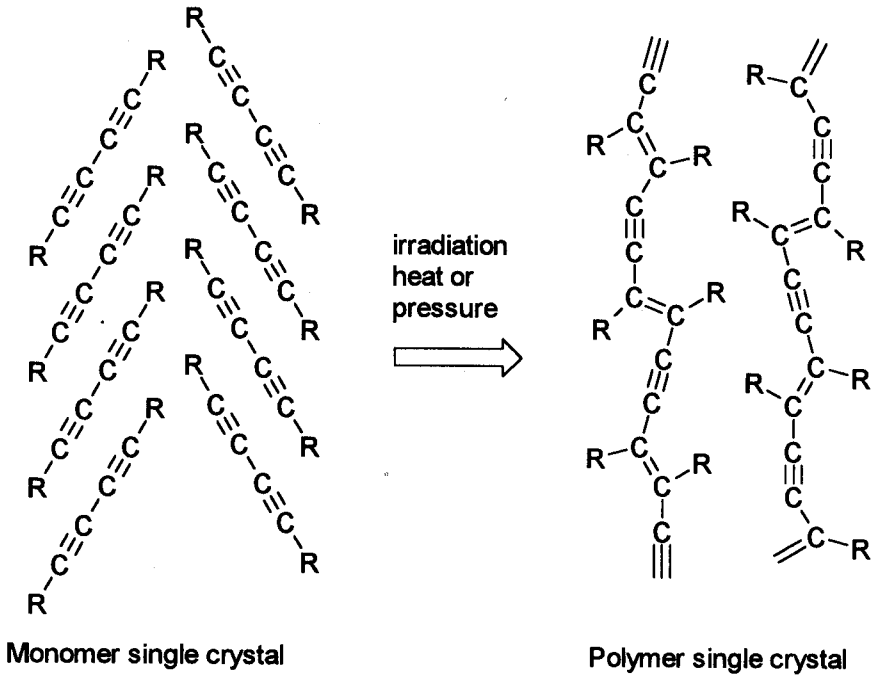


Figure 1. Topochemical polymerization of diacetylene.

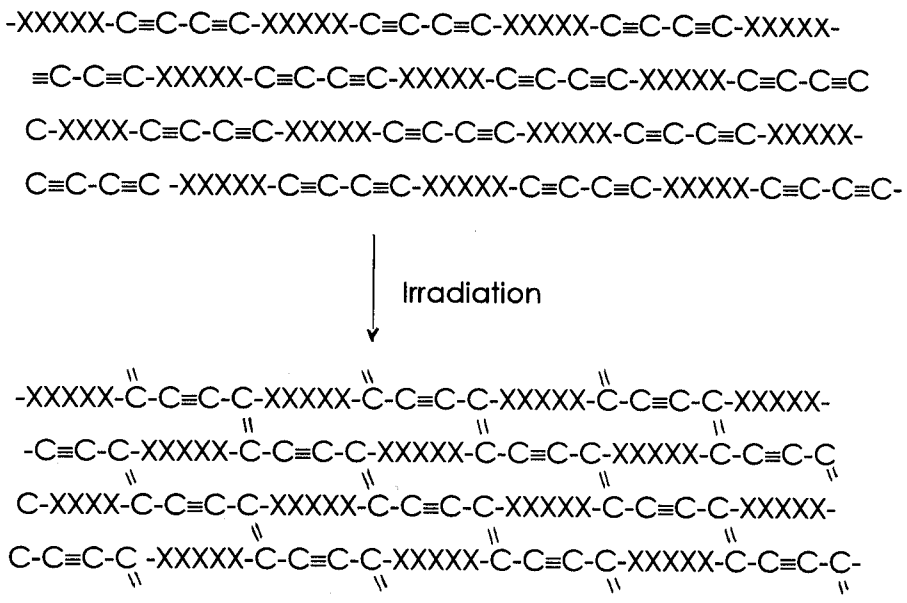


Figure 2. Schematic presentation of diacetylene-containing polymers. A: Before irradiation, B: After irradiation. XXXXX: Spacer group.

ty, crystallinity and reactivity of DA groups.

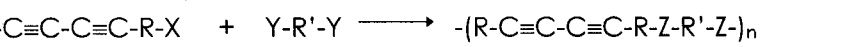
Another very important point of the oxidative coupling polymerization of bisacetylenic monomers, is the optimum polymerization condition. In the earlier reports, the polymerization conditions were adopted from the Eglinton's work[7] in which pyridine was commonly used as solvent and reactions are carried out at room temperature, thus obtaining low molecular weight polymers. In recent studies, $N,N,N'N'$-tetramethylethylenediamine is used as a base,[8] and the polymerization conditions have been improved using proper solvents which dissolve the polymers formed, and at temperatures around 60–80°C,[9] and thus high molecular weight polymers are readily obtained.

On the other hand, the oxidative coupling reaction of terminal acetylenes using cuprous salts and bases, is an old reaction,[10] and has been investigated by many.[11] Various speculations have been made on the mechanisms, although not totally established. The mechanism seems to differ depending on the reaction conditions. Because of the importance of copolymerization, oxidative coupling reactions of 5 different acetylenes were carried out under the optimum conditions for polymerization in order to predict the compositions of copolymers, and the results are reported in this article. Results of copolymerization of a few systems are also reported.

2 Experimental

Synthesis of acetylenes: The reagents employed were supplied by Aldrich, and they were used as received. The reaction products were properly purified and characterized by FT-IR and ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectroscopy (Varian). 3-Butynyl-N-n-butylcarbamate (U), bp. 73°C/0.1 mmHg, was prepared from n-butylisocyanate and 3-butyn-1-ol. 3′-Ethynyl-n-butylbenzamide (**A**), mp. 26–27°C, was synthesized by the reaction of n-butylamine with 3-ethynylbenzoyl chloride which was prepared by the Heck reaction of trimethylsillyl acetylene with 4′-bromomethylbenzoate. Propargylbenzoate (**B**) was obtained by the reaction of propargyl alcohol with benzoyl chloride. Phenyl acetylene (**P**)

1. Direct polymerization of functional monomers.



X, Y = reactive functional groups. Z = Reaction product of X with Y.

2. Oxidative coupling polymerization.

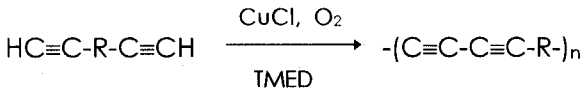


Figure 3. Synthetic routes of diacetylene-containing polymers.

and 1-octyne (**O**) were distilled before use.

Coupling reactions: All the oxidative coupling reactions of two different acetylene were carried out under same conditions: 1:1 molar ratio of each acetylene (2.5–6.3 mmoles), 0.07 g CuCl (purified), 0.5 ml of tetramethylethylene diamine (TMED), and 13–15 ml of *N*-methylpyrrolidone, at 75°C for 2.5 hours with a constant oxygen flow. After the reaction the system was poured into dilute hydrochloric acid, and the precipitated product was washed with water and dried. It was necessary to separate the three products by column chromatography. Identification of each diacetylene was made by thin layer chromatography, FT-IR and ^{1}H and ^{13}C NMR spectroscopy.

Photoreactivity measurement: The diacetylenes were irradiated with UV light from a medium pressure 400 W UV lamp of Ace Glass to see the relative reactivities.

3 Results and Discussion

(1) Oxidative coupling between 3′-ethynyl-*n*-butylbenzamide (**A**) and 3-butynyl-*N*-*n*-butylcarbamate (**U**).

$$\mathbf{A} + \mathbf{U} \longrightarrow \mathbf{A}\text{–}\mathbf{A} + \mathbf{U}\text{–}\mathbf{U} + \mathbf{A}\text{–}\mathbf{U}$$

One of the products was insoluble in warm acetone, and it was filtered off, washed with acetone, and recrystallized from ethanol. This was found to be **A–A** from FT-IR and ^{1}H and ^{13}C NMR spectra. Its yield was 25.5%. The rest 74.5% was mixture of **A–U** and **U–U**, and it was not possible to separate them by column chromatography because their solubilities were too similar to each other, and therefore their respective yields were not available. **A–U** was synthesized by Cadiot-Chodkiewikcz coupling to study its photoreactivity:

$$m\text{–}CH_3(CH_2)_3\,NH\text{–}{}^5CO\text{–}Ph\text{–}{}^1C\,{}^2C\text{–}{}^3C\,{}^4C\text{–}CH_2CH_2O\text{–}6\,CO\text{–}NH(CH_2)_3\,CH_3$$

A–U

^{13}C NMR spectra(δ): ^{1}C: 80.08, ^{2}C: 70.99, ^{3}C: 67.13, ^{4}C: 88.24, ^{5}C: 170.93, ^{6}C: 168.10.

(2) Oxidative coupling between the urethane (**U**) and propargyl benzoate (**B**).

$$\mathbf{U} + \mathbf{B} \longrightarrow \mathbf{U}\text{–}\mathbf{U} + \mathbf{B}\text{–}\mathbf{B} + \mathbf{U}\text{–}\mathbf{B}$$

The overall yield of coupling was 73%. One of the products could be separated by recrystallization from a benzene/hexane mixture, which was found to be **U–U**. The other two were satisfactorily separated by column chromatography using benzene as eluent, the first elueted being **B–B**. **U–U**: IR(KBr, cm^{-1}); 3300(N–H), 2243 and 2150 (C≡C–C≡C), 1695(O=C), 1540(N–C). ^{1}H NMR: no signal of 2.63 ppm of C≡C–H remaining. ^{13}C NMR(δ): 66.09(1) and 77.39(2) of [R–C(2)≡C(1)]$_2$. **B–B**: IR(KBr, cm^{-1}) 3050 (C–H *ar*), 2200 and 2145 (C≡C–C≡C), 1730 (O=C), 1605 (C–H *ar*), 1260 (C–O–C). ^{1}H NMR: signal of H-C≡C– no longer present. ^{13}C NMR(δ) for [R–C(2)≡C(1)]$_2$ at 69.62 (1) and 75.36 (2). **U–B**: IR(KBr, cm^{-1}) 3335 (N–H), 3045 (C–H *ar*), 2250 and 2170 (C≡C–C≡C), 1723 (C=O *ester*), 1690 (C=O *urethane*), 1600 (C-C *ar*), 1538 (N–H), 1250 (C–O–C). ^{13}C NMR (d); 165.18 (*ar*–C=O), 156.02 (–O–C=O–NH–). 64.93, 70.86, 71.24 and 79.92 (C≡C–C≡C, not assigned individually).

Table 1 shows the results indicating that B is more reactive than U.

(3) Oxidative coupling between the amide (**A**) and the benzoate (**B**).

$$\mathbf{A} + \mathbf{B} \longrightarrow \mathbf{A}\text{–}\mathbf{A} + \mathbf{B}\text{–}\mathbf{B} + \mathbf{A}\text{–}\mathbf{B}$$

The overall yield of coupling was 90.5%. **A–A** was extracted with warm acetone, and the others were separated by chromatography using benzene as eluent. The first eluted was **B–B**, followed by **A–B**. They were characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The **A–A** and **B–B** of this coupling were the same as that obtained by the previous coupling reactions between **A** and **U**, and **U** and **B**, respectively. **A–B**: IR(KBr, cm^{-1}): 3230 (N–H), 2240 (C≡C–C≡C), 1727 (C=O *ester*), 1630 (C=O *amide*), 1540 (N–C), 1265–1260 (C–O–C). ^{13}C NMR(δ): 133.80 (C=O *amide*), 134.73 (C=O *ester*), 70.00,

Table 1. Yields of coupling reaction between the urethane (**U**) and the benzoate (**B**).

Acetylenes	Reacted (mole)	Remaining (mole)	% Reacted
U	0.00360	0.00265	57.6
B	0.00533	0.00092	85.8

Products	Amount (mole)	Yield (%)
U–U	0.00104	24.00
B–B	0.00191	41.67
U–B	0.00153	34.43

Table 2. Yields of coupling reaction between the amide (**A**) and the benzoate (**B**).

Acetylenes	Reacted (mole)	Remaining (mole)	% Reacted
A	0.00158	0.0009	63.7
B	0.00170	0.00078	68.5

Products	Amount (mole)	Yield (%)
A–A	0.00037	25.08
B–B	0.00043	23.22
A–B	0.00085	51.69

Table 3. Yields of coupling reaction between the urethane (**U**) and phenylacetylene (**P**).

Acetylenes	Reacted (mole)	Remaining (mole)	% Reacted
U	0.00384	0.00177	68.4
P	0.00431	0.0013	76.8

Products	Amount (mole)	Yield (%)
U–U	0.00128	39.71
P–P	0.00152	28.31
U–P	0.00129	31.98

Table 4. Yields of coupling reaction between the urethane (**U**) and n-octyne (**O**).

Acetylenes	Reacted (mole)	Remaining (mole)	% Reacted
U	0.0033	0.0017	66
O	0.0033	0.0016	67

Products	Amount (mole)	Yield (%)
U–U	0.000833	27.9
O–O	0.000856	23.4
U–O	0.001598	48.65

73.05, 78.13, 78.34 (C≡C–C≡C not assigned individually). The respective yields are shown in Table 2. It can be seen that the reactivities of **A** and **B** are similar to each other, but unsymmetric coupling seemed to be preferable.

(4) Oxidative coupling between the urethane (**U**) and phenylacetylene (**P**).

$$\mathbf{U} + \mathbf{P} \longrightarrow \mathbf{U\text{–}U} + \mathbf{P\text{–}P} + \mathbf{U\text{–}P}$$

The symmetric product **U–U** was readily separated by treatment with warm hexane in which it was insoluble. It was identical to those obtained in the previous two couplings. **P–P** and **U–P** were separated by column chromatography, the first fraction (**P-P**) with benzene as eluent and the second (**U–P**) with a mixture of benzene and chloroform (30/70% in volume). They were confirmed to be pure from their FT-IR, ^{1}H and ^{13}C NMR spectra. **P–P**: IR(KBr, cm^{-1}); 3100 (C-H *Ar.*) 2150 (C≡C–C≡C), 1605 (C–C *Ar.*). ^{1}H NMR(δ); 7.43 (m, 3H, *m*- and *p*-) and 7.62 (dd, 2H, *o*-). **U-P**: IR(KBr, cm^{-1}); 3335 (N–H), 3100 (C-H *ar.*), 2250 and 2170 (C≡C–C≡C), 1695 (C=O), 1530 (N–C), 1225 (CO–C). ^{13}C NMR(δ); 82.68, 65.57, 73.99 and 75.01 for –CH_2-^{1}C^{2}C-^{3}C^{4}C–Ph, respectively. The overall yield of the coupling was 87%, and the respective yields of each product are shown in Table 3. No appreciable preference in coupling was observed.

(5) Oxidative coupling between the urethane (**U**) and 1-octyne (**O**).

$$\mathbf{U} + \mathbf{O} \longrightarrow \mathbf{U\text{–}U} + \mathbf{O\text{–}O} + \mathbf{U\text{–}O}$$

U–U was separated by the method of the previous case. **O–O** and **U–O** were separated by column chromatography using benzene as eluent to obtain the former and a benzene/acetone mixture (7/3) to elute the latter. The overall yield was 80%. The respective yields of each product and the moles of reacted and remaining acetylenes are shown in Table 4. The reactivities of **U** and **O** were similar to each other, but unsymmetric coupling was more preferable to the symmetric couplings.

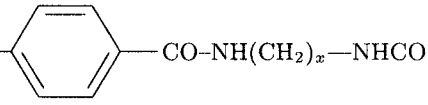
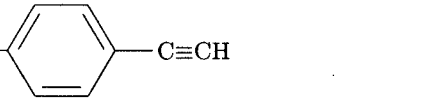
It can be said from these results that among these acetylenes employed in this work, there was no remarkable difference in the oxidative coupling reaction, although in a few cases unsymmetric coupling appeared to be more dominant. Bohlmann et al.[12] have reported that a donor acetylene such as 1-hydroxypent-2-en-4-yne, **X**, showed a very low reactivity when coupled with phenylbutadiyne, **Y**, and with phenylacetylene, **Y′**, (**X–X**: 0.1%, **X–Y**: 0.3%, **Y–Y**: 99.6%, and **X–X**: 10.5%, **X–Y′**: 38.5%, **Y′-Y′**: 51%). In this work, aromatic acetylenes, **A** and **P**, showed no such high reactivities compared to the propargylic and alkyl acetylenes. This is probably because there is not enough difference in electronic density for the

Table 5. Some physical and chemical characteristics of the diacetylenes obtained by the unsymmetric oxidative coupling reactions.

Diacetylenes	Appearance	Melting point (°C)	Sensitivity to UV light*	Color after irradiation
U–U	Fibrous	236–238	+++	Purple
A–A	Fine needless	240–241	++	Blue
B–B	Powder	66–68	+	Red
P–P	Fine crystals	82–83	—	
O–O	Liquid	—	—	
U–A	Powder	147–149	+	Violet
U–B	Fine crystals	60–62	+++	Purple
A–B	Powder	131–133	+	Yellow
U–P	Powder	47–48	+	Violet
U–O	Powder	34–35	++	Deep Orange

*This photosensitivity is a qualitative expression determined by exposing crystals to UV irradiation for different periods to develop coloring: +++: highly sensitive (10 min); +: slightly sensitive (100 min); ++: moderately sensitive (70 min); -: not sensitive (over 100 min).

Table 6. Oxidative coupling copolymerization of diamides with a diurethane.

DA: $HC{\equiv}C$–  –$CO{-}NH(CH_2)_x{-}NHCO$–  –$C{\equiv}CH$

DA-6, DA-7, DA-10 and DA-12: x = 6, 7, 10 and 12, respectively.
DU: $HC{\equiv}C{-}(CH_2)_2{-}O{-}CONH{-}(CH_2)_6{-}NHCO{-}O{-}(CH_2)_2{-}C{\equiv}CH$.

Copolymers (mole/mole)	[a]Inherent viscosity (η)	[b]Melting temp. °C	[c]DA Polym. temp. °C	[d]Degradation temp. °C	[e]Color after irradiation
Poly(DA-6-*co*-DU) 25:75	0.38	—	230	240	Purple
Poly(DA-7-*co*-DU) 25:75	0.34	—	242	199	Light violet
Poly(DA-7-*co*-DU) 75:25	0.30	—	240	300	Light blue
Poly(DA-10-*co*-DU) 50:50	0.38	—	200–247	329	Violet
Poly(DA-12-*co*-DU) 25:75	0.38	185	250	293	Purple

a) dl/g, determined in NMP at room temperature. b) — no melting. c) Determined from DSC. The first is starting temp. and the second is the peak maximum temp. d) Determined from TGA. e) Electron beam irradiation.

pairs chosen, or the reaction conditions of this work are quite different from those of the Bohlmann's paper.[12] It is expected that the more acidic the acetylenic proton of the compounds, the more reactive in the coupling. However, N,N'-tetramethylethylenediamine is a stronger base than pyridine thus being capable of abstracting acetylenic protons with low acidities. The reactivity probably differs depending on the reaction conditions, and therefore the mechanism appears to be not as simple as those reported previously with a free radical[13] and ionic[12] mechanisms.

Some of the physical and chemical properties of these new diacetylenes are shown in Table 5. The urethane-containing diacetylenes were found to be more photosensitive than others, but no other regularity in the photoreactivity was observed among these diacetylenes, as the reactivity is solely controlled by their respective lattice structures.

It can be also predicted that random copolymers will be obtained by the oxidative coupling copolymerization of the corresponding bisacetylenes, and block copolymers will not be obtained. The results of copolymerization of aromatic amide with urethanes are shown in Table 6. The copolymerization improved the solubility of polymers because the ho-

mopolyamides are insoluble in organic solvents. The polymers were semicrystalline, and their films are opaque. It is worth mentioning that the polymers are radiation sensitive as they developed coloring by radiation, but they are not heat sensitive below the melting points. Such materials can be candidates for radiation sensor for radiotherapy and radiation detectors.

4 Conclusion

The results obtained in this work indicated that there is no significant difference in oxidative coupling selectivity of the acetylenic compounds with different resonance stability and electronic density, all of them showing more or less similar reactivities to each other. The resonance effect seems to be not important because aromatic acetylene such as phenyl acetylene did not show a significant difference in coupling ability from aliphatic acetylenes employed in this work. However, it may be necessary to couple two acetylenic compounds with a large difference in electronic density between them, in order to see if a significant selectivity would be observed or not. It can be said therefore, that random copolymers are expected to form by copolymerization of different bisacetylenic monomers.

Acknowledgment

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