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PREPARATION OF POLYDIACETYLENES WITH PURE ALIPHATIC SUBSTITUENTS

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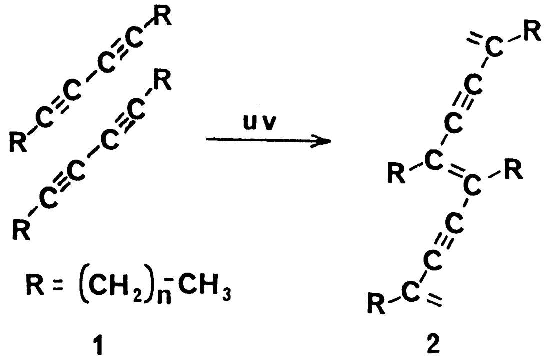
Diacetylenes, $R-C\equiv C-C\equiv C-R$, ($R = -(CH_2)_n-CH_3$, n=5,7,9), were irradiated with UV light or γ-ray, yielding red polymers, $[=(R)C-C\equiv C-C(R)=]_x$, of which structure was confirmed by the Raman spectroscopy.

Solid-state polymerization of diacetylenes has attracted attention in a point that the polymerization gives a fully conjugated crystalline polymer1) or polymeric multilayer.2) Diacetylenes polymerize in the solid-state either on thermal annealing or on exposure to high energy irradiation. These polymers are generally insoluble and infusible. Therefore, they suffer disadvantages that polymer-processing or polymer characterization is difficult. Modification of the substituents of the diacetylenes gives organic solvent-3) or water-soluble polymers.4) Until recently, however, polydiacetylene with pure aliphatic substituent has not yet been prepared. We have found that some diacetylenes having long aliphatic substituents polymerize on exposure to UV light to give soluble polymers.



1 2

	n	mp/°C		yield/%
a	5	-25– -23	a	not determined
b	7	-1 – 0	b	28
c	9	17 – 18	c	23
d	11	37 – 39	d	0

Diacetylenes prepared in the present study were 1a – d. These monomers except for 1d were polymerized in a Petri dish cooled at -78 °C by irradiating with UV light for 0.5 h, yielding red polymers, of which the molecular structures were investigated by the Raman spectroscopy. At the early stage of the polymerization the monomers became blue and finally turned to deep red. Unpolymerized monomers were extracted with hot benzene. The yields were determined by weighing the residue. Though monomer 1b was sealed in a glass tube and irradiated with γ-ray at -78 °C, the yield did not exceed 20%. Monomer 1d turned to light yellow-green on exposure to γ-ray at room temperature but gave no polymer.

These polymers were slightly soluble in tetralin or carbon tetrachloride. Polymer 2b, which was obtained by the radiation polymerization, serves as a representative example. The X-ray diffraction pattern of the powdered sample did not exhibit any peak, thus showing that 2b is an amorphous polymer. Its DSC curve (5 °C/min) possessed an endothermic peak due to melting at 167 °C on heating and an exothermic peak at 159 °C on cooling. The intrinsic viscosity, [η], in tetralin at 135 °C was 0.48 (dl/g). The absorption spectrum of a carbon tetrachloride solution showed a broad band with a maximum around 475 nm.

It was difficult to obtain the Raman spectra of insoluble polydiacetylenes, because of decomposition resulting from the laser excitation.[5,6] However, the Raman spectrum of a diluted carbon tetrachloride solution of 2b gave strong bands at 2117 and 1517 cm^{-1} with 514.5 nm source, which are assigned to ν(C≡C) and ν(C=C), respectively. The Raman spectroscopy provides a powerful means of investigating the structure of soluble polydiacetylene.[7]

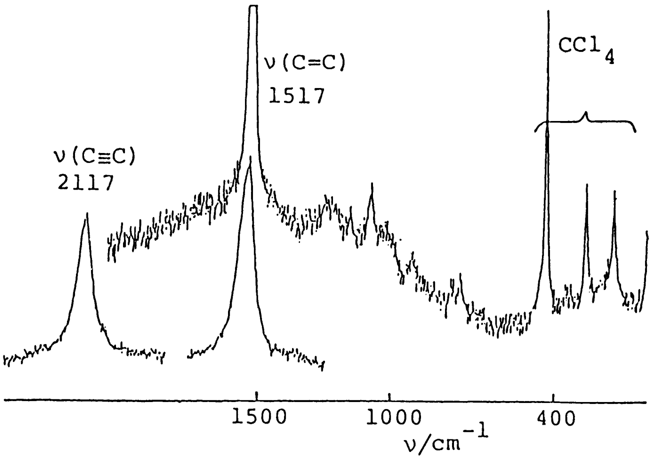


Fig. 1. Raman spectrum of 2b in CCl_4, 514.5 nm excitation.

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