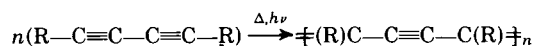


NOTES

Copolymerization of Diacetylenes in the Crystalline Solid State. A Method for Recording Latent Fingerprints

INTRODUCTION

Disubstituted diacetylenes $R-C\equiv C-C\equiv C-R$, where R is a substituent group, are a unique class of compounds that polymerize in the crystalline solid state upon thermal annealing or upon exposure to ionizing radiation.¹⁻³ The polymerization occurs via 1,4-trans addition reaction:



The synthesis and the solid-state polymerization of a number of diacetylenes have been reported in the literature.¹⁻⁸ Recently, Enkelman¹⁴ has reported polymerization of mixed diacetylene crystals. A large number of vinyl monomers and ring compounds have been polymerized in the solid state.⁹ Ring compounds such as trioxane and phosphonitrilic chloride polymerize to crystalline polymers by so-called topotactic reaction, whereas vinyl monomers such as acrylamide and methacrylic acid generally lead to amorphous polymers. A systematic disordering of the crystalline monomer phase occurs during polymerization. Some of these compounds have been copolymerized in the solid state.^{10,11} Monomers having similar chemical constitutions or crystalline lattices can form uniform solid solutions or a eutectic mixture. In order to obtain copolymerized diacetylenes, we cocrystallized a number of diacetylenes having similar chemical constitution. In the present paper, we report on the solid state copolymerization of 2,4-hexadiyn-1,6-bis(phenylurethane), referred to hereafter as HDDPU, and 2,4-hexadiyn-1,6-bis(*p*-chlorophenylurethane), referred to hereafter as HDD_pCPU.

Human perspiration consists primarily of water, inorganic salts (NaCl), amino acids, and oils. This secretion is transferred from the ridges of the fingers or the palm to any surface touched by the hands. The water portion of this secretion evaporates, leaving colorless residues of oils, amino acids, and inorganic salts on the surface. This all but invisible, though highly characteristic, surface impression is called a latent fingerprint. Latent fingerprints must be "developed" into a clearly visible form. At present this is done by spraying a solution of ninhydrin, spraying a solution of silver nitrate, or brushing a powder over a suspected area of contact.¹² Ninhydrin reacts with amino acid residues to form compounds red or violet in color. Silver nitrate reacts with sodium chloride residues forming silver chloride which then reduces to silver, yielding a highly visible black color. Lightly brushed powders adhere to deposited oils or grease. In each case the ridge impressions become visible lines. It is also shown that a solution of HDDPU containing 2% to 20% by weight of HDD_pCPU is useful in detecting latent fingerprints.

EXPERIMENTAL

HDDPU and HDD_pCPU were synthesized using a method described by Wegner.¹³ The diacetylenes were cocrystallized by rapid precipitation from solution. Specifically, 10 ml of solutions of HDDPU containing different mole fractions of HDD_pCPU in acetone were poured dropwise into hexane under continuous stirring at room temperature (RT) and at -70°C . The cocrystallized diacetylenes were filtered and dried under vacuum. The cocrystallized compositions were polymerized by thermal annealing at 40°C for 26 hr and by ^{60}Co γ -ray at RT. Polymer conversion was determined by extracting unreacted monomer with acetone.

RESULTS AND DISCUSSION

HDDPU and HDD_p CPU cocrystallize into active (polymerizable) and inactive (unpolymerizable) phases. They cocrystallize into an inactive phase (white) if the precipitation temperature is below ca. -40°C, preferably -70°C. The inactive phase does not polymerize upon thermal annealing or upon exposure to ionizing radiation. The diacetylenes cocrystallize into an active phase if the precipitation temperature is above ca. 0°C.

Polymerization of the active phase is almost instantaneous as evidenced by development of a blood-red color within a few minutes at RT. The red color intensifies with time and temperature of annealing. The copolymerized compositions appear metallic above ca. 15% polymer conversion. The initial rate of polymerization of the active phase is so high that it cannot be determined by the conventional methods, as some of the cocrystallized compositions turn dark red (about 5% polymer conversion) by the time the precipitates are filtered and dried under vacuum. The rates of polymerization of the cocrystallized compositions were assessed from polymer conversions. HDDPU cocrystallized at different mole fractions of HDD_p CPU was dried under vacuum over night (16 hr at RT). A portion of the cocrystallized compositions was annealed at 40°C for 26 hr while the other portion was irradiated with ⁶⁰Co γ-rays at RT. Figure 1 shows plots of polymer conversion versus mole fraction of HDD_p CPU. The rate of polymerization is maximum at 0.1 mole HDD_p CPU. It is interesting to note that HDDPU and HDD_p CPU alone are almost thermally inactive but the cocrystallized compositions (>0.3 mole fraction of HDD_p CPU) are highly reactive.

The homopolymers and the copolymers are insoluble in common organic solvents. Formation of copolymer is suggested by IR studies. IR spectra of HDDPU and HDD_p CPU are very similar, except for the presence of an unidentified band at 1405 cm⁻¹ in HDD_p CPU. This band is absent in HDDPU. The ratio of intensity of the 1405 cm⁻¹ band to that of the 1705 cm⁻¹ band (used as an internal standard) was used as a measure of HDD_p CPU in the copolymers and the corresponding cocrystallized mixtures. The results suggest that the composition of the copolymer formed in the solid state is similar to the initial composition of the cocrystallized mixture. This is not surprising for this pair of diacetylenes because the rates of homopolymerization of HDDPU and HDD_p CPU are almost the same.

It was discovered accidentally that when a solution of HDDPU containing about 2% to 20% HDD_p CPU by weight is sprayed on an oily surface, the diacetylenes cocrystallize into an inactive phase. This phase does not polymerize thermally or by exposure to high energy radiation; it remains white. Sprayed on a clean surface, the diacetylenes cocrystallize into a highly reactive phase. This active phase polymerizes readily at room temperature, producing a red or violet color. Thermal annealing or high-energy radiation increases the degree of polymerization and yields a correspondingly more intense color.

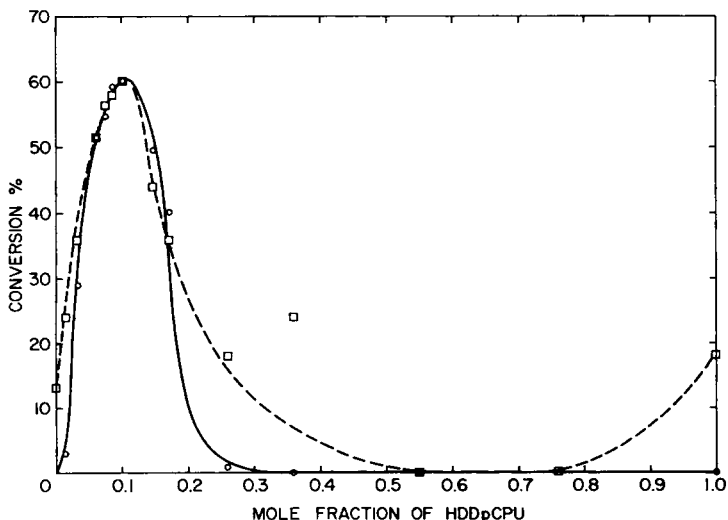


Fig. 1. Plot of percent copolymer vs mole fraction of HDD_p CPU. Cocrystallized diacetylenes were polymerized by annealing at 40°C for 26 hr (solid line) and by irradiating with ⁶⁰Co γ-rays at RT for 15 Mrads (broken line): (□) γ radiation; (○) thermal.

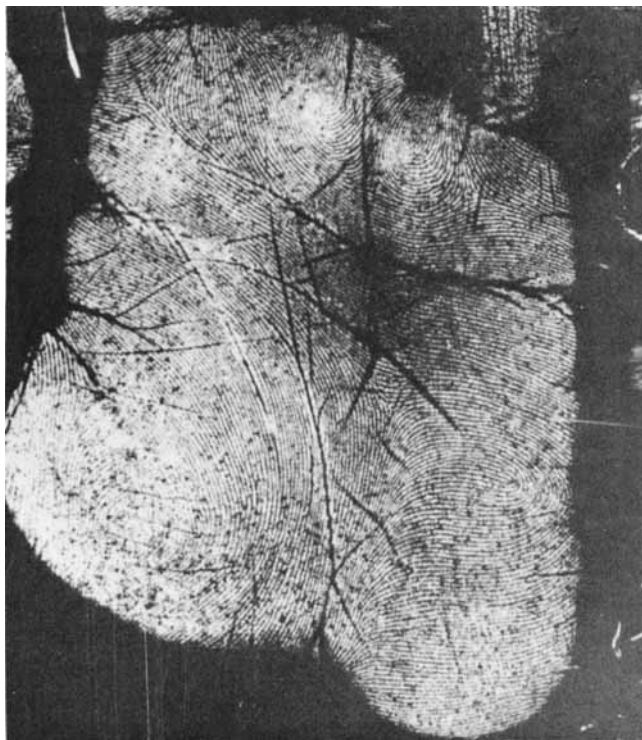


Fig. 2. Palm prints detected on a plastic film by spraying a solution of HDDPU containing 10% by weight of HDD_pCPU, followed by thermal development.

When this diacetylene solution is sprayed over latent fingerprints, the inactive phase forms where oily residues exist and the active phase forms where there is no oil. Development of visible fingerprints takes 10 min at room temperature, 1 min at 120°C. A typical example is shown in Figure 2. Ridge impressions are white while the spaces between are red, violet, even black or metallic gold depending upon the degree of polymerization in this active phase. HDDPU also copolymerizes with 2,4-hexadiyn-1,6-bis(*p*-bromophenylurethane), HDD_pBPU, in the solid state with the maximum rate of polymerization at a mole ratio of 9:1. A solution of HDDPU containing 2% to 20% by weight of HDD_pBPU is also useful in detecting latent fingerprints. In contrast to the copolymerized compositions mentioned above, HDDPU does not copolymerize with 2,4-hexadiyn-1,6-bis(*p*-fluorophenylurethane).

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