Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Some Comments on Experimental Aspects of the Use of Ionizing Radiation to Initiate Solid State Reactions

V. Shivshankar [a], Hyunjoo Moon [a] & Daniel J. Sandman [a]

[a] Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, 01854-2881, U.S.A.

Version of record first published: 04 Oct 2006

To cite this article: V. Shivshankar, Hyunjoo Moon & Daniel J. Sandman (1998): Some Comments on Experimental Aspects of the Use of Ionizing Radiation to Initiate Solid State Reactions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 367-371

To link to this article: http://dx.doi.org/10.1080/10587259808044301

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 367–371
Reprints available directly from the publisher
Photocopying permitted by license only

Some Comments on Experimental Aspects of the Use of Ionizing Radiation to Initiate Solid State Reactions

V. SHIVSHANKAR, HYUNJOO MOON, AND DANIEL J. SANDMAN
Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts 01854-2881 U.S.A.

Abstract. Examples are given of organic crystals undergoing solid state reaction initiated by ionizing radiation where the properties of the product, especially surface morphology, obtained differ depending on specific experimental conditions. The authors strongly recommend that researchers using ionizing radiation for synthetic purposes specify experimental conditions used, especially the atmosphere over the sample and the radiation dosage and dose rate.

INTRODUCTION

Ionizing radiation has been a major tool for the initiation of solid state reactions, especially polymerization, at least since the 1951 report of the interaction of an electron beam with ethyleneglycol dimethacrylate.[1] The penetrating character of the ionizing radiation to all matter allows processes to occur that do not occur, for example, with uv radiation. While uv light can initiate solid state polymerization of diacetylene(DA) monomers, the stronger absorption of the initially formed polymer prevents complete monomer-to-polymer conversion unless the thickness of the experimental sample allows penetration of the light. To obtain completely polymerized bulk single crystals of the melt-stable dialkylurethanes of 5,7-dodecadiyn-1,12-diol(1a-c), it is necessary to use ionizing radiation.[2] To obtain bulk single crystals of the polydiacetylene (PDA, 1)) of 1,6-di-N-carbazolyl-2,4-hexadiyne(DCH), it is necessary to use ionizing radiation, as the thermal process converts single crystal monomer to polycrystalline polymer.[3]

In the use of ionizing radiation for synthetic purposes, it is important to keep in mind the range of reactions that can be initiated by radiation. The interaction of ionizing radiation with the atmospheric gases nitrogen and oxygen leads to the formation of ozone and the oxides of nitrogen.[4] Hence, it is important to know if an irradiation was performed on a sample in the presence of air or on an evacuated sample. For the specific case of DA monomers, it is appropriate to recall that ozone and oxides of nitrogen can initiate polymerization

in the absence of radiation.[5] Additionally, solids prepared by crystallization from solution can include solvent in crystalline defects, and this included solvent can initiate reactions that would otherwise not occur,[6-8] especially when the solvent contains heavy atoms such as chlorine.

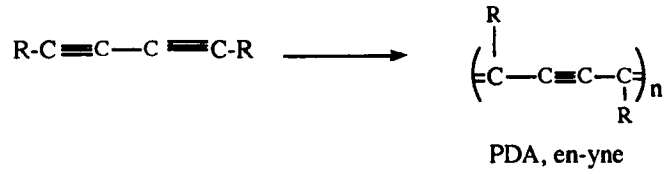
Nevertheless, in spite of the reactivity of ionizing radiation toward virtually anything, many publications that report the use of radiation in synthetic experiments do not detail the specific experimental conditions under which an irradiation was performed. Specifically, one does not know what total dose was used, what dose rate was used, or what was the nature of the atmosphere above the sample undergoing irradiation. A parameter such as dose rate is important because the rate of product formation in radiation-induced chain processes depends on it.[9]

The preparation of this report was motivated by three different experiments carried out in our laboratories in recent years that revealed an important difference in the product of an irradiation depending on whether the process was carried out in the presence or absence of air. This is especially critical for crystals of interest for their linear and nonlinear optical properties, such as PDA. In such crystals, light interacts first with the crystal surface. Hence the quality of the surface is of paramount interest for such crystals. We summarize this experimentation here in the hope that other experimenters will detail specific experimental conditions involved when ionizing radiation is used for bulk synthetic experiments. Scheme 1 shows the experimental systems under discussion and an illustration of the diacetylene polymerization.

RESULTS AND DISCUSSION

We have recently reported[10] that Atomic Force Microscopy(AFM) studies of single crystals of diacetylene(DA) monomers that are dialkylurethanes of 5,7-dodecadiyn-1,12-diol reveal anisotropic surface eruptions on the [100] faces of these crystals when they are irradiated with ^{60}Co γ radiation or electron beams in the presence of air, but not in its absence. The eruptions on the average are 0.5 microns at the base and about 700 Å in height. They appear after about 1 Mrad of radiation in a process requiring about 50 Mrad for complete conversion to polymers that are thermochromic and reported[11] to be photochromic. Crystals having surface eruptions are irreversibly converted from their blue form to a red form at room temperature on exposure to a single pulse of 532 nm light while crystals lacking the eruptions do not undergo this change. Hence, the interaction of these crystals with laser light is critically dependent on the surface

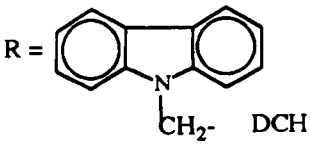
morphology of the crystals, and that, in turn, depends on the specific details of the irradiation process.



PDA, en-yne

R = $-(CH_2)_4$-O-C(O)-NH-R', 1

R' = $-C_2H_5$, ETCD, 1a
R' = i-C_3H_7, IPUDO, 1b
R' = n-C_3H_7, PUDO, 1c



X-C≡C-$(CH_2)_8$-C(O)-NH_2

X = H, 10-undecynamide
X = Br, 11-bromo-10-undecynamide

Scheme 1. Molecular structures under discussion and illustration of the diacetylene polymerization.

In additional recent work[12], we have found that the surface morphology of PDA-DCH crystals, as revealed by micron-scale AFM study, depends on whether or not the polymerization is carried out in the presence of air. For polymerization carried out in the absence of air, the [100] face of PDA-DCH crystals[13] reveals a generally smooth fibrous morphology. In the presence of air, the [100] surface of the crystals is markedly less fibrous and reveals regions where significant etching has occurred. A typical etched surface region is displayed in Figure 1. Such etching was not observed in our studies of the alkylurethanes already reported.[10] Ozone and oxides of nitrogen would be less reactive toward the aliphatic groups and urethane groups that are near the [100] surface of the thermochromic PDA crystals[10] than they would be toward the carbazole groups exposed by the morphology of PDA-DCH crystals.[13]

A third system studied recently is 11-bromo-10-undecynamide.[14] Our interest in this compound followed from our earlier crystallographic and spectroscopic studies of the solid state reactivity of monoacetylenes, particularly 10-undecynamide.[15] In spite of crystallographic C-C contacts between potentially reactive acetylenic carbons as short as 3.66 and 3.75 angstroms[15],

10-undecynamide is unreactive on exposure to 50 Mrad doses of ^{60}Co γ-radiation in either the absence or presence of air. For 10-undecynamide, excitation at all wavelengths between 120-300 nm leads to light emission at wavelengths greater than 300 nm.[15]

In the interest of enhancing the reactivity of a crystalline monoacetylene via a heavy atom effect, we synthesized 11-bromo-10-undecynamide.[14] 11-Bromo-10-undecynamide is reactive toward both 254 nm uv light and ^{60}Co γ-radiation. In the latter case, the product is an amorphous polyacetylene. When 11-bromo-10-undecynamide is irradiated with 50 Mrad ^{60}Co γ-radiation in the absence of air at ambient temperature, the product obtained is a dry solid, m.p. 66-71°C, while a similar irradiation in the presence of air leads an oily solid, m.p. 55-71°C. Both solids have a similar conversion to polymer.[14] The crystal structure of 11-bromo-10-undecynamide[16] reveals that the interaction between acetylene groups is different than that of 10-undecynamide.

CONCLUSIONS

Above, we have discussed three monomeric systems that undergo solid state polymerization under the influence of ionizing radiation, especially ^{60}Co γ-

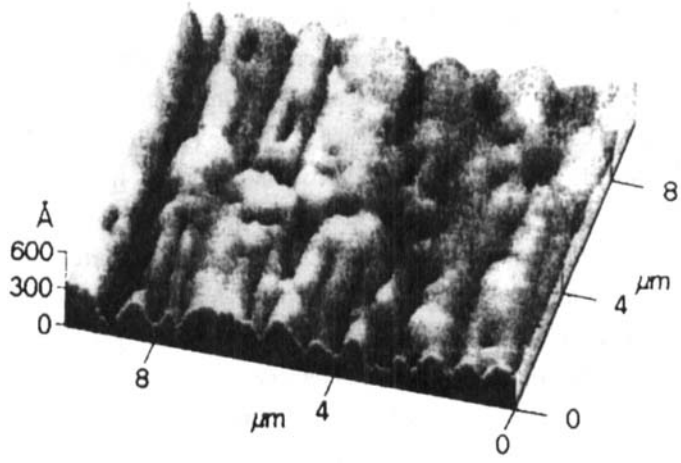


Figure 1. AFM image of the [100] face of a PDA-DCH single crystal polymerized by ^{60}Co γ–radiation(60Mrad) in the presence of air.

radiation. The properties of the products are clearly dependent on whether the irradiation was performed in the presence or absence of air. This is particularly important for crystals of interest for their linear and nonlinear optical properties such as PDA. Accordingly, we recommend to investigators who use ionizing radiation for synthetic purposes that they specify as much experimental detail as is meaningful to someone who might attempt to repeat their experiments. Considerations such as temperature, total radiation dosage, radiation dose rate, and the nature of the atmosphere above the sample are clearly very important.

ACKNOWLEDGEMENTS

This work was supported in part by the U.S. Air Force Office of Scientific Research under Grant F49620-1-0179. The authors thank Ms. Mary Montesalvo for facilitating access to the radiation source at the University of Massachusetts Lowell.

REFERENCES

1. D.J. Sandman and P. Cukor, Mol. Cryst. Liq. Cryst., 105, 1-10(1984).
2. V. Enkelmann, Adv. Polym. Sci., 63, 91(1984).
3. (a) V. Enkelmann, G. Schleier, G. Wegner, H. Eichele, and M. Schwoerer, Chem. Phys. Lett., 52314-319(1977); (b) K.C. Yee and R.R. Chance, J. Polym. Sci., Polym Phys. Edit., 16, 431-441(1978).
4. J.W.T. Spinks and R.J. Woods, *An Introduction to Radiation Chemistry*, 2nd edition, John Wiley & Sons, New York, 1976, pp.217-219.
5. G.N. Patel, H.R. Battacharjee, and A.F. Preziosi, J. Polym. Sci., Polym. Lett. Ed., 19, 511(1981).
6. J.E. Herz and V. Stannett, J. Polym. Sci., Polym. Lett. Ed., 4, 995(1966).
7. D.J. Sandman, G.P. Hamill, L.A. Samuelson, and B.M. Foxman, Mol. Cryst. Liq. Cryst., 106, 199-217(1984).
8. D.J. Sandman, B.S. Elman, G.P. Hamill, C.S. Velazquez, and L.A. Samuelson,Mol. Cryst. Liq. Cryst., 134, 89-107(1986).
9. J.W.T. Spinks and R.J. Woods, *An Introduction to Radiation Chemistry*, 2nd edition, John Wiley & Sons, New York, 1976, pp.187-191.
10. V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, Acta Polymer., 48, 88-91(1997).
11. S. Koshihara, Y. Tokura, K. Takeda, T. Koda, Phys. Rev. Lett., 68, 1148(1992).
12. V. Shivshankar, Ph.D. Thesis, University of Massachusetts Lowell, 1997.
13. V. Enkelmann, R.J. Leyrer, G. Schleier, and G. Wegner, J. Mater. Sci., 15, 168-176(1980).
14. H. Moon, M.S. Thesis, University of Massachusetts Lowell, 1997.
15. D.J. Sandman, C.S. Velazquez, G.P. Hamill, B.M. Foxman, J.M. Preses, and R.E. Weston, Jr., Mol. Cryst. Liq. Cryst., 156, 103-108(1988).
16. B.M. Foxman, private communication.