CHEMISTRY LETTERS, pp. 589-592, 1981.

TRIBOLUMINESCENCE AND TRIBOPOLYMERIZATION OF 9-ETHYL-3-VINYLCARBAZOLE

Takashi INOUE and Shigeo TAZUKE
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

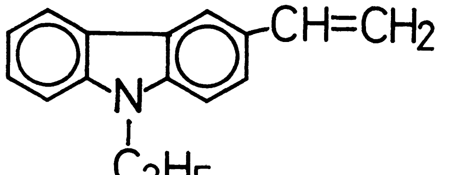
9-Ethyl-3-vinylcarbazole(I) was found to be triboluminescent as well as tribopolymerizable in crystalline state. When mechanical stress was applied to I crystals, the observed luminescence was identified as fluorescence by comparing with photoexcited emission from the crystals and also by energy transfer to singlet excited state of perylene. Tribopolymerization was confirmed by GPC analysis. Although correlation between triboluminescence and tribopolymerization was not clear, friction induced thermal polymerization was unlikely and the singlet excited state of I was tentatively considered as the precursor of initiating species.

We are now reporting unusual finding that crystals of 9-ethyl-3-vinylcarbazole(I) emit luminescence under mechanical stress and furthermore polymerizes simultaneously. These phenomena were found accidentally in the course of preparing I as a starting material for photoconductive polymers. There are a number of examples on triboluminescence which have been interpreted by several assumed mechanisms[1]. To the best of our knowledge, however, the correlation of triboluminescence with possible subsequent chemical reactions has not been explored.

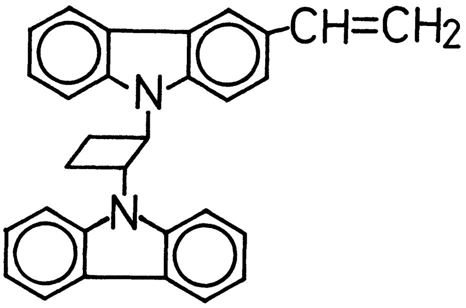
Crystals of I emit light on shaking in a glass vessel, rubbing on a hard surface, or grinding in a mortar. The triboluminescence spectra are shown in Fig. 1 in comparison with conventional photoexcited luminescence. The triboluminescence(Fig. 1a) is identical to that of solid state fluorescence from I crystals excited at 360 nm(Fig. 1b). The shape of Fig. 1b is independent of the wavelength of excitation so that the spectrum is considered to be characteristic of the crystals. Energy transfer behaviors in the tribo- and the photo-excited state of I are also identical. The I crystals obtained by evaporating chloroform solution of I doped with 5 mol% of perylene were examined for the luminescence characteristics. Photo- and triboluminescence shown in Fig. 1c and 1d, respectively, consists mostly of perylene fluorescence[2] while the emission by I is quenched, indicating that the triboluminescent state of I is the singlet excited state.

While I crystals are being ground in a mortar, the appearance changes from micro-crystalline to tacky amorphous state. GPC analysis shown in Fig. 2 confirms polymer formation. Although mechanochemical reactions involving polymers are well established as represented by radical formation during polymer breakdown and rubber kneading[3], there seems to be a minimum requirement of polymer chain length for the reactions to occur. It is consequently very unlikely that radicals are produced directly from a low molecular weight vinyl compound by the action of mechanical stress.

Analogous reactions to the present tribopolymerization might be found in the field of lubrication. Thin polymer film deposition on wearing metal surface(friction polymer)[4] has been reported to occur when prepolymers and/or monomers are added to a lubricant. The reaction conditions are,



(I)



(II)

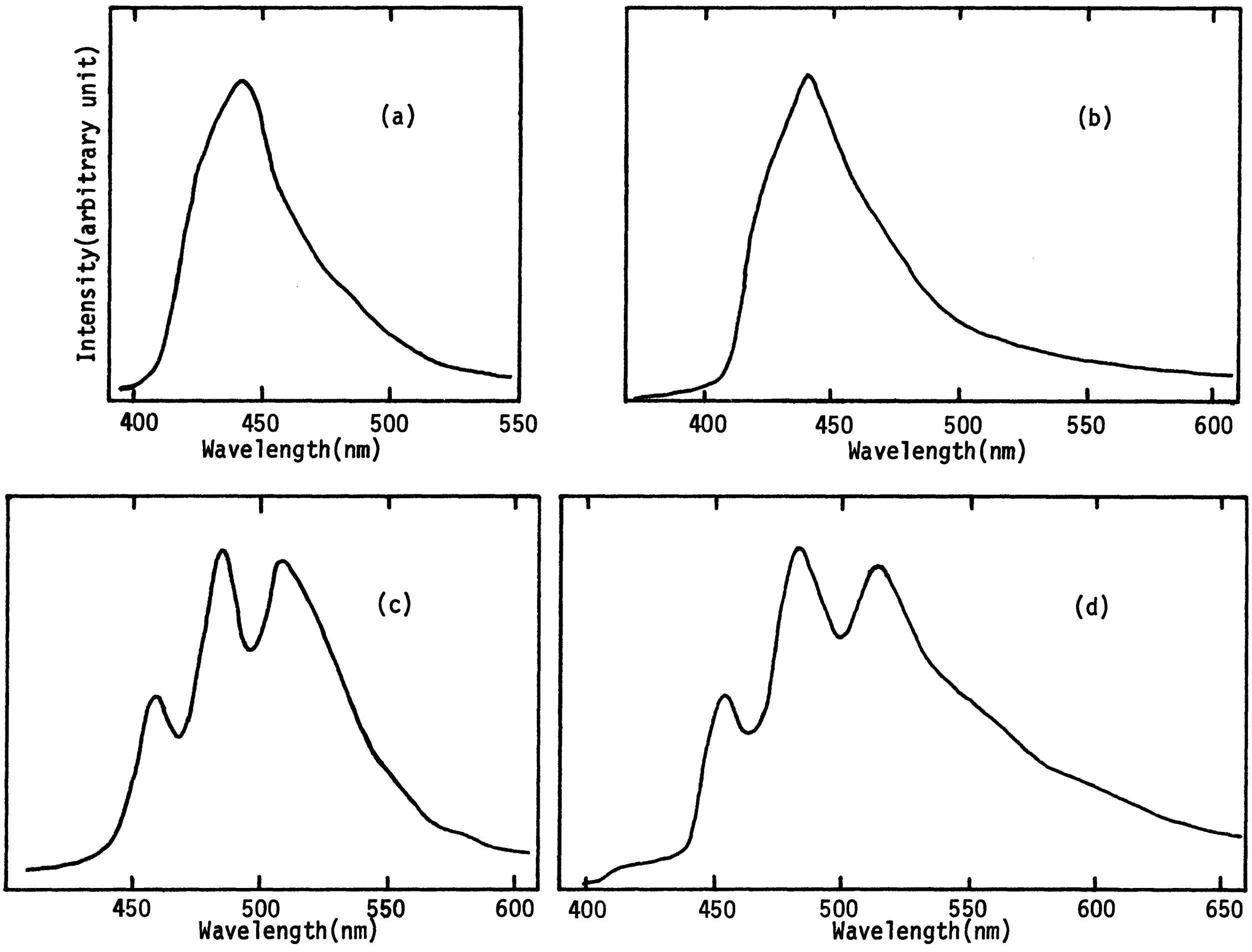


Fig. 1. Luminescence of I crystals.
a) triboluminescence, b) photo-induced fluorescence, c) and d) triboluminescence and photo-induced fluorescence in the presence of perylene, respectively.

however, so severe that the temperature on the metal surface is said to go up to 300-700°C. The polymer deposition is therefore probably of thermal origin. Under the present experimental conditions of grinding manually, thermal polymerization brought about by friction heating is unconceivable. Furthermore, compression of I in a KBr disk maker for IR spectroscopy induces polymerization as well, which denies the possibility of thermal polymerization.

This tribopolymerization system is complicated by simultaneous tribodegradation of polymers formed tribochemically. GPC analysis after different grinding time indicates that high molecular weight polymers formed during the initial period are fragmented with increasing the grinding time as shown by the shift of GPC peak to a lower molecualr weight region together with the broadening of molecular weight distribution.

The polymerization mechanism has not been explored yet. We consider tentatively that the mechanically produced singlet state is responsible for the formation of initiating species. In support of this, photoirradiation of I crystals in air with a high pressure mercury lamp induced polymerization. Generation of singlet excited state is sensitive to the structure of vinyl compound. A vinyl derivative of trans-1,2-dicarbazolylcyclobutane(II) is neither triboluminescent nor tribopolymerizable. The electronic energy levels of II should not be much different from those of I. Difference in their crystal structures might therefore be responsible for this.

Experimental

9-Ethyl-3-vinylcarbazole(I). The reported preparation procedure[6] was modified slightly as follows. In the course of the Wittig reaction of 9-ethyl-3-formylcarbazole, methylsulfinyl carbanion in DMSO[5] was used instead of n-butyllithium in THF. Triphenylmethylphosphonium bromide was first treated with methylsulfinyl carbanion and then added with 9-ethyl-3-formylcarbazole. After usual workup, the crude product was chromatographed on an alumina column(eluent: n-hexane - benzene). Yield was 94% which was considerably higher than the reported value[6]. m.p. 68.0-68.5° (Lit.[6] 66-67°), E.A. (%) Found(Calcd): C87.08(86.84), H6.77(6.83), N6.33(6.31), NMR(δ/$CDCl_3$): 1.4(t, J=7.0Hz, 3H, CH_3), 4.3(q, J=7.0Hz, 2H, $-CH_2-$), 5.2(d, J=10.4Hz, 1H, vinyl), 5.7(d, J=17.4Hz, 1H, vinyl), 6.9(d.d, J=10.4 and 17.4Hz, 1H, vinyl).

Luminescence measurements. Since triboluminescence is an instantaneous phenomenon and quantitative repetition is not possible, spectrum recording must be accomplished within a single event. For this purpose, a spectrometer equipped with an optical multi-channel analyser(OMA) or a multichannel photodiode(MCPD) detector may be useful. The former has a higher sensitivity and a longer gate opening time(3 s) than the latter so that manually operated triboluminescence is easily synchronized with the gate opening time. An OMA equipped with a Vidicon detector SIT S20(Princeton Applied Research Inc.) was connected to a monochrometer, UFS 200 flat field spectrograph(grating 200 grooves/mm, Jobin Ivon Inc.). Solid I was rubbed in a quartz vessel in front of the monochrometer slit and emitted light was monitored. Conventional photoluminescence was measured by a Hitachi MPF-4 spectrophotometer. The spectra were corrected for the wavelength dependence of photomultiplier.

Tribopolymerization. The monomer I was ground in a mortar and then analyzed for polymer formation by a GPC(Toyo Soda Kogyo Co. Ltd. HLC-802UR, column: G4000HS + G2500H, solvent: chloroform, temperature: 40°C).

Acknowledgement

We are greatly indebted to Professor A. Sawaoka, Research Laboratory of Engineering Materials, of our Institute who permitted us to use the OMA equipped spectrometer.

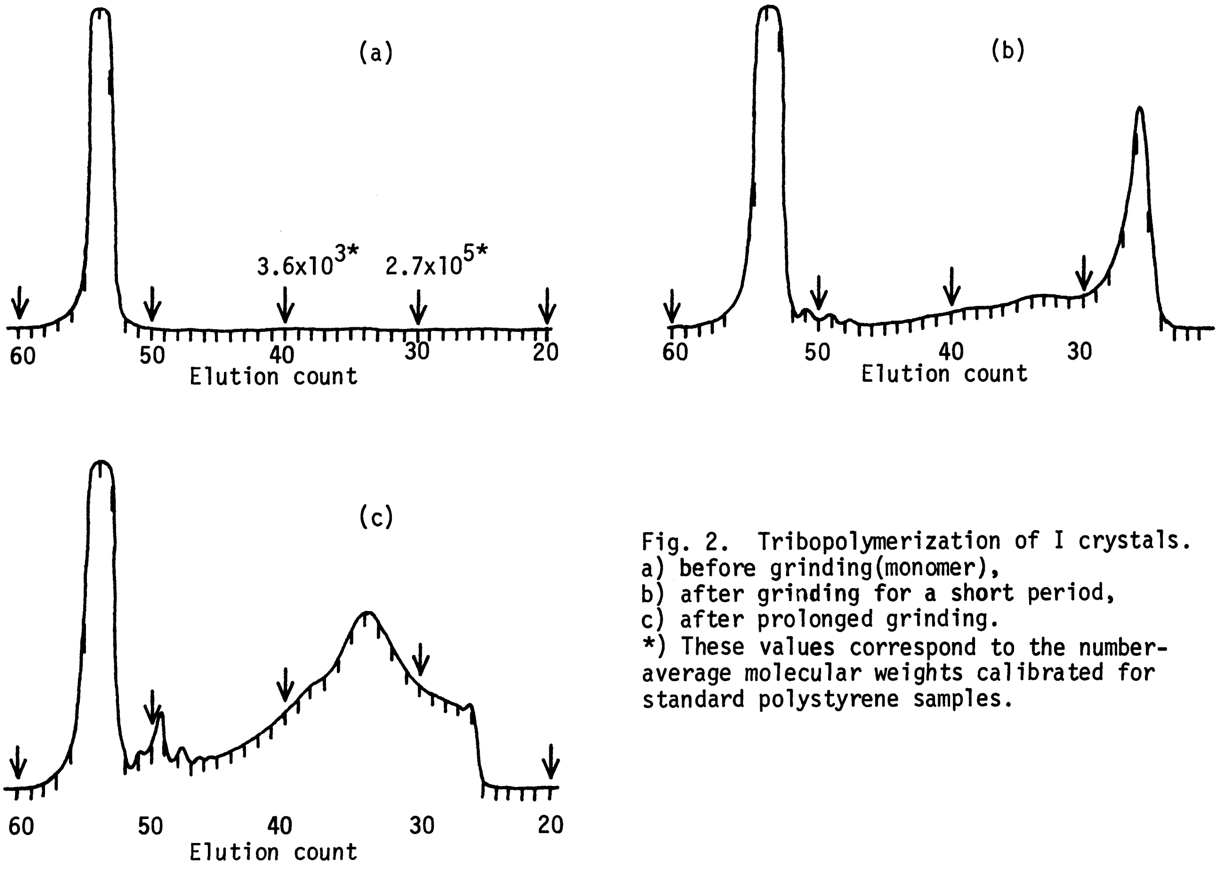


Fig. 2. Tribopolymerization of I crystals.
a) before grinding(monomer),
b) after grinding for a short period,
c) after prolonged grinding.
*) These values correspond to the number-average molecular weights calibrated for standard polystyrene samples.

References and Notes.

1) a) J. I. Zink, Acc. Chem. Res., 11, 289(1978), b) S. H. Lin, D. Wutz, Z. Z. Ho, and H. Eyring, Proc. Natl. Acad. Sci. USA, 77, 1245(1980), c) A. J. Walton, Adv. Phys., 26, 337(1977).

2) The spectra shown in Fig. 1c and 1d are different from photo-induced fluorescence of perylene single crystal. Although the spectra are broad, three emission peaks characteristic of perylene fluorescence in solution are observed in the solid state luminescence. The broadening is a common trend of solid state luminescence. The doped perylene to I is therefore considered to be dispersed nearly monomolecularly in or on I crystals.

3) a) E. H. Andrews and P. E. Reed, "Molecular Fracture in Polymer" (Advances in Polymer Science 27), S. S. Sternstein, Ed., Springer Verlag, Berlin, 1978, p48. b) H. H. Kausch, "Polymer Fracture", Springer Verlag, Berlin, 1978, p87.

4) a) S. W. Chaikin, Wear, 10, 49(1967), b) M. J. Furey, Wear, 26, 369(1973).

5) R. Greenwald, M. Chaykovsky, and E. J. Corey, J. Org. Chem., 28, 1128(1963).

6) W. W. Limburg and D. J. Williams, Macromolecules, 6, 787(1973).

7) The photophysical and photoconductive behavior of the polymers prepared from these monomers are now in the course of investigation.

(Received February 18, 1981)