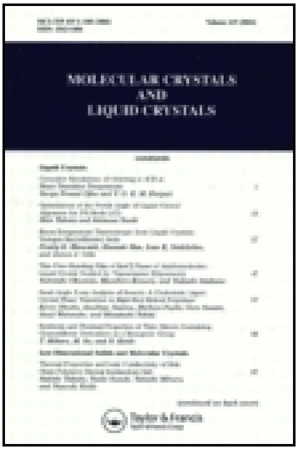

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Formation and Deactivation of Extremely Long-Lived Charge-Separated Species in Carbazolyl Vinyl Polymers Absorbed on Macroreticular Resin

Hiroshi Miyasaka [a] , Tomoko Ota [a] , Shoji Kotani [a] & Akira Itaya [a]

[a] Department of Polymer Science and Engineering, Kyoto Institute of Technology, Sakyo, Kyoto, 606, JAPAN E-mail:

Version of record first published: 04 Oct 2006

To cite this article: Hiroshi Miyasaka, Tomoko Ota, Shoji Kotani & Akira Itaya (1998): Formation and Deactivation of Extremely Long-Lived Charge-Separated Species in Carbazolyl Vinyl Polymers Absorbed on Macroreticular Resin, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 193-198

To link to this article: http://dx.doi.org/10.1080/10587259808044331

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 193–198
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in India.

Formation and Deactivation of Extremely Long-Lived Charge-Separated Species in Carbazolyl Vinyl Polymers Absorbed on Macroreticular Resin

HIROSHI MIYASAKA, TOMOKO OTA, SHOJI KOTANI and AKIRA ITAYA
Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Sakyo, Kyoto 606, JAPAN (E-mail, miyasaka@ipc.kit.ac.jp)

Dynamics of formation and deactivation processes was discussed for extremely long-lived (>8h) charge-separated states following photo-induced electron transfer in carbazolyl vinyl polymers, poly(N-vinylcarbazole), poly(7-vinylbenzo[c]carbazole, and poly(5-vinylbenzo[b]carbazole), coadsorbed with 1,2,4,5-tetracyanobenzene as an electron acceptor on a macroreticular resin, Amberlite XAD-8, at room temperature.

Keywords: electron transfer; photoconductive polymer; poly(N-vinylcarbazole); poly(N-vinylbenzocarbazole)

INTRODUCTION

Electron transfer (ET) reaction is ubiquitous in nature and artificial systems[1-6]. In nature, one of the most representative systems where ET reactions take place systematically and efficiently is a photosynthetic reaction center in plants. In this natural system, photoinduced charge separation is followed by sequential charge shift reactions (electron transport) in three-dimensional arrangements of pigments, resulting in the formation of the long-lived charge-separated (CS) state. A number of investigations have been performed[5,6] to construct artificial assemblies closer mimic of complicated chromophore compositions where long-lived CS states are attained.

For the production of the long-lived CS systems, it seems intriguing to utilize aromatic vinyl polymers as a component, since some of these macromolecules have photoconductive properties attributable to the sequential charge-shift reactions among the pendant aromatic groups[7]. Under the condition where rather long inter-ionic distance attained by the charge shift reaction is fixed, the long-lived CS state after the photoinduced CS may be attained. Along this line, we reported in previous papers[8,9] that the CS state was observed even at 8 hours after the excitation at room temperature in the PVCz adsorbed on macroreticular resins with an electron acceptor. In order to obtain the detailed information on the formation of the long-lived CS state, we have investigated the dynamic behaviors of the ET processes of various aromatic vinyl polymers adsorbed on the macroreticular resin in the present work.

EXPERIMENTAL

For the detection of the dynamic behaviors, transient diffuse reflectance absorption spectra were measured using a microcomputer-controlled nanosecond laser photolysis system[10] with an excimer laser (351 nm, 20 ns fwhm, 11 mJ/cm^2) as an excitation source.

Poly(5-vinylbenzo[b]carbazole) (P5VBCz)[11], poly(7-vinylbenzo[c]-carbazole) (P7VBCz)[11] and 1,2,4,5-teracyanobenzene (TCNB : Wako GR Grade) were respectively purified by usual methods. Acrylic macroreticular resin, Amberlite XAD-8, (Rohm & Haus, mean pore diameter = 225Å, grain size = 250-850 nm), was purified[8,9] before use. Structure of XAD-8 is shown in Fig. 1, where R is the methylene chain (-CH$_2$- or -CH$_2$-CH$_2$-). Each polymer and TCNB were adsorbed on XAD-8 from their 1,2-dichloroethane solution

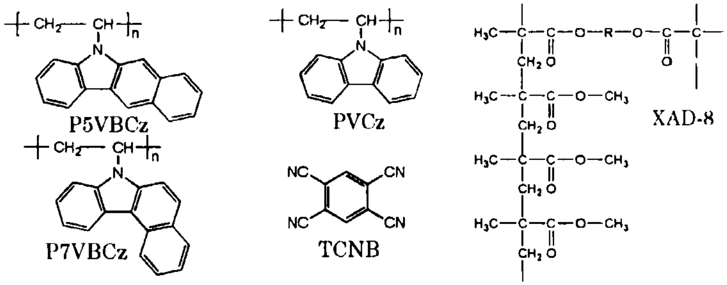

FIGURE 1 Molecular structures of compounds used.

and then the adsorbents were dried under vacuum. The pore radius of the macroreticular resin is almost the same as the radius of the gyration of the polymer in 1,2-dichloroethane solution. Hence, each polymer chain seems to be separately adsorbed on XAD-8. Even if more than one chain is adsorbed on one pore, it should be remarked that the photoinduced ET reactions such as CS, hole transfer (HT) and charge recombination (CR) take place in a finite space. All the measurements were performed under vacuum at 296 K.

RESULTS AND DISCUSSION

Fig. 2 shows transient absorption spectra of P5VBCz- and P7VBCz-TCNB adsorbed on XAD-8, observed at several tens of minutes following the excitation with a 351 nm excimer laser pulse at 296 K. As a reference, the result of PVCz-TCNB[8,9] is also exhibited. Each spectrum shows the absorption peak at 465 nm, which is safely ascribed to the anion of TCNB (TCNB$^-$)[8,9]. On the other hand, broad absorption in the wavelength region above 600nm is respectively assigned to the cation radical of each polymer[8,9,12]. This figure indicates that the extremely long-lived CS state is produced also in P5VBCz- and P7VBCz-TCNB systems, as in the PVCz-TCNB system[8,9]. Since such a long-lived ionic species was observed also by

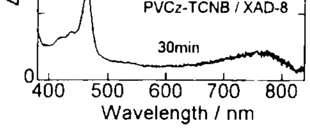

FIGURE 2 Transient absorption spectra of P5VBCz-, P7VBCz- and PVCz-TCNB on XAD-8 systems at 296K, excited with a nanosecond 351 nm laser pulse.

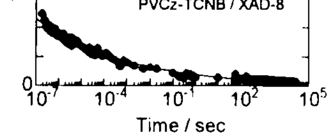

FIGURE 3 Time profiles of the CS states of P5VBCz-, P7VBCz- and PVCz-TCNB on XAD-8 systems, monitored at TCNB$^-$ absorption. A solid line in each frame is the calculated result based on Eqs. (1)-(2) (see text).

the steady-state irradiation with *ca.*350 nm light of Xe-lamp, the production of the long-lived ionic species is not attributable to multiphoton ionization process. In addition, it was confirmed that the charge separation in the excited singlet state is responsible for the production of the ionic species[9].

In the time region < 1 s, the decay of the cation radical was identical with that of the anion for each of three systems, indicating that the disappearance of the ionic species is due to the charge recombination (CR) process. On the other hand, the decay of the absorption signal of the cation in hours time region was slightly faster than that of the anion. This result implies that the decomposition of the cation radical of each aromatic group takes place to some extent in hours time region. The portion of the decomposition was, however, estimated to be < 15% of the decay of the cation in longer time region. Hence, it is concluded that the main pathway of the deactivation is CR process between the cation of each aromatic group and $TCNB^{-}$. From the temperature dependence on the decay profiles, it was found that the long-distance electron tunneling was responsible for the charge recombination in the long time region[8,9]. The formation of the ion pair with rather long inter-ionic distance was attributed to the hole-migration process along the polymer chain and the trapping process of the hole to fix the inter-ionic distance.

On the basis of the long-distance electron transfer, the time profiles of the CS state were analyzed by following equations:

$$\Delta A(t) \propto \sum_i P(r_i) \cdot \exp\left[-k_{CR}^0 \exp(-\tfrac{r_i}{\alpha}) \cdot t\right] \qquad (1)$$

$$P(r_i) = \exp(-r_i / \beta) \qquad (2)$$

Here, ΔA is the transient absorption intensity and $P(r_i)$ is the population of the CS states after the hole was trapped at the appropriate site with the inter-ionic distance, r_i. When the hole migration takes place along the polymer chain after the initial charge separation between A^- and D_0^+ and the detrapping process of the hole is ignored, the number of the hole trapped at D_i is proportional to $p(1-p)^i$. In the calculation, the β value corresponding to p=0.22 was employed.

The time profiles of the CS state monitored at 465 nm are plotted in Fig. 3. The result of PVCz-TCNB[8,9] is also shown as a reference. The solid line in each flame is a curve calculated by eqs. (1) and (2). Each parameter in the calculation was set to be identical among these three systems, except for the k^0_{CR} value, for which 1.5-2.0 times larger values were assumed for the P5VBCz- and P7VBCz-TCNB systems than that for the PVCz one. Although the large deviation between the experimental results and the calculated curve is observed in shorter time region, the experimental results on and after 10^{-5} s following the excitation for the P5VBCz- and P7VBCz-TCNB systems are well reproduced by the calculated curve as in the PVCz-TCNB system. This result clearly demonstrates that the same mechanism as that in the PVCz-TCNB system is responsible for the formation of the long-lived CS state also in the P5VBCz- and P7VBCz-TCNB systems.

In order to obtain information on the origin of the large deviation in the time region $<10^{-5}$s, we have measured the time profile of the charge transfer (CT) emission of the P5VBCz-TCNB system. The CT emission is observed mainly for the CR between the anion and the neighboring cation, since the exchange interaction in the ion pair plays an important role in the radiation process of the CT emission. Hence, the detrapping process from the shallow trap site resulting in the CR between the anion and the neighboring cation is required for the radiation of CT emission. The time profile $f(t)$ of the CT emission (recombination emission), due to the CR process is expressed by

$$f(t) \propto \frac{dp(t)}{dt} \tag{3}$$

where $p(t)$ is the population of the CS state. By assuming that both time functions are in proportion with t^m (the power low of time, t) in narrow time window, m values for the $f(t)$ and $p(t)$ (corresponding to ΔA(t)-C(t), where C(t) is the calculated time profile as mentioned above.) were respectively obtained to be -1.9 and -0.84. That is, the difference in the m values between the $f(t)$ and $p(t)$ is ~1. This indicates that the eq. 3 holds for the present experimental results, and hence it is strongly suggested that the deviation is attributable to the detrapping process resulting in the CR between the anion and the neighboring cation. Similar time profiles were also observed for the P7VBCz-TCNB system.

Finally, we briefly discuss the origin of the trap site. In aromatic vinyl polymers, it is widely known that various dimer cations are effectively produced and the hole is trapped at the dimer cation sites. However, the CR time profile in the time region on and after ca. millisecond region was not affected by the tacticity of the polymer[9] nor the kind of polymer. Hence, the deep trap site for the hole was not simply ascribable to the dimer cation sites. Rather, it may be attributed to the aromatic groups adsorbed in the vicinity of the polar ester groups. Actually in the similar adsorbent system to XAD-8 one, where the polar ester group exists but the approach of the Cz groups to it is hindered by bulky long alkyl chain around the ester groups, such a long-lived CS state was not detected[9]. This result also supports the idea that the "solvated" aromatic moieties in polar environments play an important role as a trap site in the production of the long-lived CS state in the present system.

Acknowledgment

The present work was partly supported by the Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan (Priority-Area-Research, "Photoreaction Dynamics", No. 06239107 and 08218233).

References

[1.] R.A. Marcus, N. Sutin, *Biochim. Biophys. Acta*, **811**, 265 (1985).

[2.] N. Mataga, in *Electron Transfer in Inorganic, Organic and Biological Systems: Advances in Chemistry Series 228*, edited by J. R. Bolton, N. Mataga, G. McLenden, (American Chemical Society, Washington, DC, 1991) Chap. 6 ;
N. Mataga, H. Miyasaka, *Prog. React. Kinetics*, **19**, 317 (1994).

[3.] I. Rips, J. Klafter, J. Jortner, in *Photochemical Energy Conversion*, edited by J.R. Norris, D. Meisel, (Elsevier, New York, 1988), p.1.

[4.] P. F. Barbara, W. Jarzeba, *Adv. Photochem.*, **15**, 1 (1990).

[5.] R. Wasielewski, *Chem. Rev.*, **92**, 435 (1992), and references cited therein.

[6.] K. Maruyama, A. Osuka, N. Mataga, *Pure Appl. Chem.*, **66**, 867 (1994).

[7.] J. Mort, G. Pfister, in *Electronic Properties of Polymers*, edited by J. Mort, G. Pfister, (Wiley-Interscience, New York, 1982), Chap. 6 and references cited therein.

[8.] S. Kotani, H. Miyasaka, A. Itaya, *J. Phys. Chem.*, **99**, 13062 (1995).

[9.] S. Kotani, H. Miyasaka, A. Itaya, *J. Phys. Chem.*, **100**, 19898 (1996).

[10.] M. Koshioka, H. Mizuma, K. Imagi, N. Ikeda, H. Fukumura, H. Masuhara, C. Kryschi, *Bull. Chem. Soc. Jpn.*, **63**, 3495 (1990).

[11.] K. Okamoto, M. Yamada, A. Itaya, T. Kimura, S. Kusabayashi, *Macromolecules*, **9**, 645 (1976).

[12.] T. Ota, H. Miyasaka, A. Itaya, in preparation.