

PHOTOINDUCED CHARGE TRANSFER POLYMERIZATION OF STYRENE INITIATED BY ELECTRON ACCEPTOR

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ABSTRACT

Photoinduced charge transfer polymerization of styrene (St) with electron acceptor as initiator was investigated. In case of fumaronitrile (FN) or maleic anhydride (MA) as initiator the polymerization takes place regularly, whereas the tetrachloro-1, 4-benzenequinone (TCQ), 2, 3-dichloro-5, 6-dicyano-1, 4-benzenequinone (DDQ), or tetracyano ethylene (TCNE) as initiator the polymerization proceeds reluctantly only after the photoaddition reaction. A mechanism was proposed that free radicals would be formed following the charge and proton transfer in the exciplex formed between St and electron acceptors.

INTRODUCTION

Photoinduced charge transfer polymerization of electron-acceptor monomer such as acrylonitrile initiated by electron donor initiator has been studied extensively and reviewed^[1], whereas the study on photoinduced charge transfer polymerization of styrene (St) is rather limited. Irie, et al. reported the photoinduced cationic polymerization of St in the presence of tetracyanobenzene at 30°C^[2]. Shirota, et al. reported the cationic polymerization of N-vinyl carbazole in the presence of electron acceptor and the alternating polymerization between N-vinylindole and fumaronitrile or diethylfumarate under irradiation^[3]. In this paper we reported the photoinduced charge transfer polymerization of St using electron acceptor as initiator.

EXPERIMENTAL

St was washed with 5% NaOH then distilled in vacuum to remove the inhibitor. Fumaronitrile (FN) was prepared according to reference [4], m. p. 95.5—96 °C. TCNE was prepared according to reference [5], m. p. 214—215 °C. TCQ, DDQ, and 7, 7, 8, 8-tetracyano-bezenequinone-dimethane (TCNQ) was purchased from Tokyo Kasai and used as received. The rate of polymerization R_p was determined by dilatometry using 300W medium pressure mercury arc as light source with 7 cm of distance from dilatometer at 25 °C. The conversion of polymerization was controlled at less than 5%. The UV-VIS and fluorescence spectra were recorded on Shimadzu UV-350 spectrophotometer and Hitachi M-850 fluorescence spectrophotometer respectively. The M_n and M_w were determined by GPC using THF as solvent.

RESULTS AND DISCUSSION

1. Charge transfer complexes (CTC)

CTC will be formed easily with the addition of electron acceptor into St. In the case of strong electron donor such as TCQ, DDQ, TCNE or TCNQ, a new band with longer absorption wavelength than that of St or electron acceptor was observed. From UV-VIS spectra and Benesi-Hildebrand equation [6] the maximum absorption wavelength λ_c , molar extinction coefficient ϵ_c and the equilibrium constant K_c can be calculated as shown in the Table 1.

Table 1 The values of λ_c , ϵ_c and K_c of CTC in CH_2Cl_2

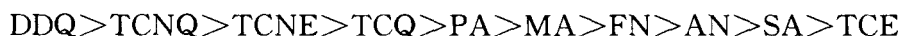
Acceptor	λ_c (nm)	ϵ_c (1/mol. cm)	K_c (1/mol)
TCQ	480	2500	0.068
TCNQ	490	7194	0.080
DDQ	535	5559	0.259
TCNE	482	820	0.690

In the cases of medium or weak electron acceptors such as maleic anhydride (MA), fumaronitrile (FN), succinic anhydride (SA) or tetrachloroethylene (TCE), a broadened absorption spectrum was observed in each case. From

the extent of broadness the relative strength of them can be evaluated roughly as in the following order $MA > FN > SA > TCE$.

2. The fluorescence of St quenched by electron acceptors

The luminascent spectrum of St with $\lambda_{\max} = 305$ nm in CH_2Cl_2 was quenched effectively and regularly by electron acceptor. From Stern-Volmer equation $I_0/I = 1 + K_q \cdot \tau \cdot [Q]$ the quenching constant $K_q \cdot \tau$ which indicates the ability of quencher can be calculated and represented in the Table 2. According to the values of $K_q \cdot \tau$ the quenching ability of different electron acceptors toward St can be arranged as follows:



It is in agreement with the strength of acceptors.

Table 2 The values of $K_q \cdot \tau$ for different electron acceptors as quencher

EA	TCE	SA	AN	FN	MA	PA	TCQ	TCNE	TCNQ	DDQ
$K_q \cdot \tau$ (1/mol)	0.8	4.4	4.5	70	140	720	4×10^2	1×10^4	1.3×10^4	2×10^4

$\lambda_{ex} = 265$ nm, $[St] = 1.95 \times 10^{-5}$ mol/L in CH_2Cl_2

3. Photoinduced charge transfer polymerization of St initiated by MA or FN as initiator

The photoinduced charge transfer polymerization of St proceeds regularly with MA or FN as initiator. The rate of polymerization R_p and the M. W. of polymer were determined and shown in the Table 3.

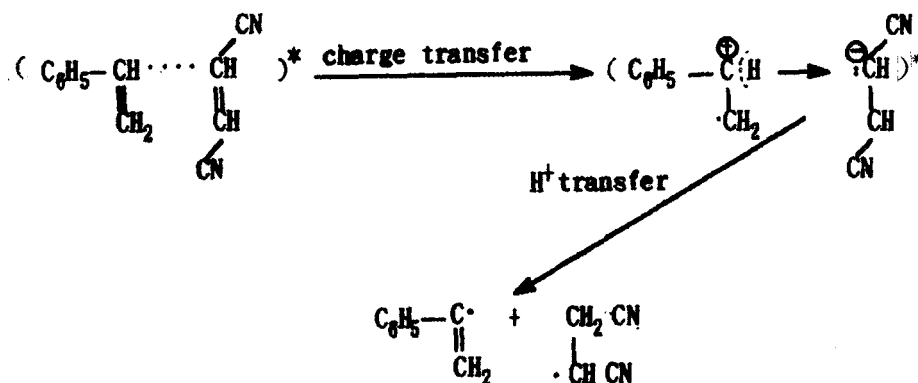
Table 3 R_p and M. W. of PSt in photoinduced polymerization of St

Electron acceptor	$R_p \times 10^5$ (mol/L · s)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$
MA	2.97	0.99	1.57
FN	1.72	1.01	1.70

300 W medium pressure mercury are at 7cm distance from dilatometer, 25°C in bulk; $[MA] = [FN] = 4.32 \times 10^{-2}$ mol/L

Referring to the initiation mechanism of photopolymerization of acrylonitrile initiated by electron donor ^[1,7], in the photopolymerization of styrene initiated by electron acceptor we propose the following initiation mechanism that the free radicals are produced from the exciplex between styrene and MA or FN under irradiation following the charge transfer and

then the proton transfer as follows:



The total result seems to be a hydrogen atom transfer from St to FN or MA. In the case of phthalic anhydride (PA) no polymerization was observed. It can be considered that although the St-PA exciplex will form under irradiation (the fluorescence of St is quenched regularly by PA, see Table 2) but the proton transfer is probably impossible to take place in St-PA exciplex because the proton transfer from St to benzene ring of PA is very difficult.

4. Photoinduced charge transfer polymerization of St initiated with TCQ, DDQ and TCNE

TCQ, DDQ and TCNE are all strong enough to form stable charge transfer complex (CTC) with St in the ground state. The colour of St changes instantly with the addition of TCQ, DDQ or TCNE due to the formation of CTC. It is important to notice that the solution colour will fade gradually under irradiation, and the polymerization will start only at the end of fading. Table 4 shows the R_p and M. W. in photoinduced polymerization of St with TCQ, DDQ and TCNE as initiators at 25°C in bulk.

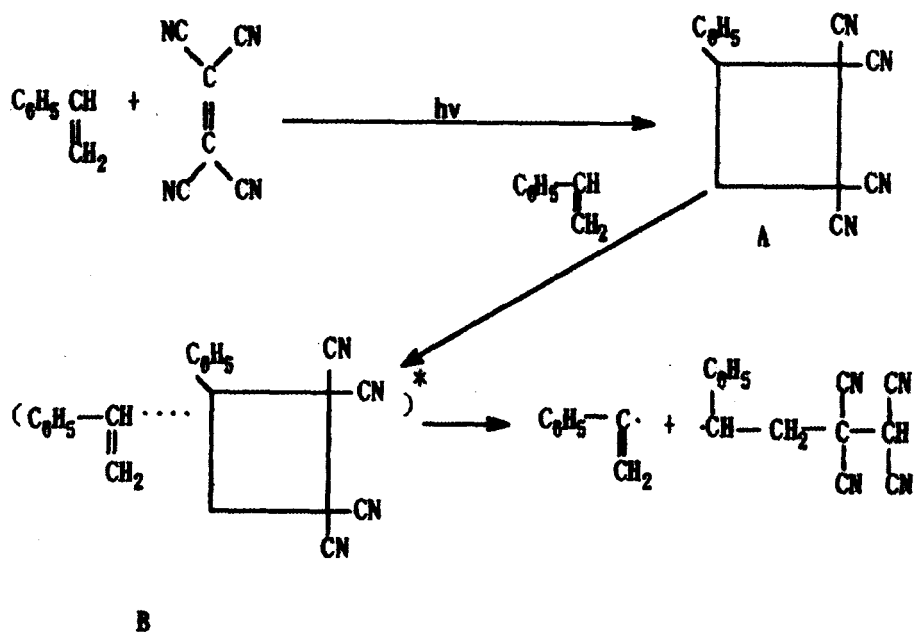
Table 4 R_p and M. W. in the photoinduced polymerization of styrene with electron acceptors

EA	[EA] (mol/L)	$R_p \times 10^5$ (mol/L. s)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$
TCQ	3.05×10^{-3}	2.75	0.506	0.233
DDQ	2.38×10^{-4}	2.28	1.260	0.684
TCNE	4.14×10^{-4}	1.52	0.451	0.214

EA: electron acceptor

We then propose the tentative mechanism in which the 2 + 2

photoaddition reaction takes place in the system of St and the strong electron acceptor such as TCNE to form quadricycle derivative A, and the exciplex B will be formed between St and A under irradiation, then the free radicals produce through the charge transfer and proton transfer as follows:



Keywords:

Styrene; Electron acceptor; Photoinduced polymerization

REFERENCES

- [1] Li, T.; Cao, W.X. and Feng, X.D., *J. Macromol. Sci-Rev, Macromol. Chem. Phys.*, C29, 1989, 154.
- [2] Irie, M.; Tomimoto, S. and Hayashi, K., *J. Polymer Sci., Part B.*, 1970, 8, 585
- [3] Shirota, Y. and Mikawa, H., *J Polymer Sci., Chem. Ed.*, 1971, 12, 2199.
- [4] Shirota, Y. and Mikawa, H., *J. Macromol. Sci-Rev. Macromol. Chem.*, C16, 1978, 129. Mowry T. and Butler, J. M., *Organic Syntheses*, 1950, 30, 46.
- [5] Linn, W.J., *Organic Syntheses, Coll.*, 1973, 5, 1008; Carboni, R. A., *Organic Syntheses Coll.* 1963, 4, 877.
- [6] Benesi, H. A. and Hildebrand, J.H., *J. Am. Chem. Soc.*, 1949, 71, 2703.
- [7] Li, T.; Cao, W.X. and Feng, X.D., *Chemical Journal of Chinese University*, 1987, 3, 52.