

## UV absorption spectra of polystyrene

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### SUMMARY

Polystyrene (PSt) exhibits a new UV absorption band at around 290nm in comparison with ethylbenzene, which is attributed to associative interaction between pendant phenyl groups. Similar absorption bands are also observed for polymers of styrene derivatives. The UV spectra suggest charge-transfer complex formation between the polymeric and monomeric donors with electron-acceptor tetracyanoethylene (TCNE) and the equilibrium constants were estimated to be in the sequence of ethylbenzene > PSt > copolymer of St with methylmethacrylate.

### INTRODUCTION

The study of effect of UV light on polymers has attracted considerable interest for many years. Spectroscopy is a fundamental part of such work. Polymers with pendant aromatic ring groups, such as PSt(1) and polyvinyl naphthalene(2), are known to show a new fluorescence band at longer wavelength under irradiation due to the interaction between excited and ground-state aromatic groups, i.e. the formation of intramolecular excimers. This phenomenon has been widely used as a powerful tool in polymer structure studies(3-6). The question arises whether a similar associative interaction could exist in the ground state. There seems to be no answer in the literature, although some authors(7) investigated charge-transfer interaction between electron-donating and electron-accepting groups on the same polymer chain. In this paper we intend to use UV spectra to examine the associative interaction among the same groups in PSt.

### EXPERIMENTAL

#### Materials

Styrene (St) was distilled under reduced pressure twice before use. Methyl methacrylate (MMA),  $\alpha$ -methylstyrene ( $\alpha$ -MSt), 4-methylstyrene (4-MSt), 4-tert-butylstyrene (t-BuSt) and ethylstyrene were distilled by standard procedures.

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### Polymerization

PSt and P4-MSt were prepared by thermal bulk polymerization at 90°C, without initiator. The copolymer of St and MMA (PSMMA) was prepared by azeotropic copolymerization of St/MMA (1/1.22).

P $\alpha$ -MSt was synthesized by cationic polymerization with BF<sub>3</sub> (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O as initiator. Pt-BuSt was prepared by bulk polymerization initiated by AIBN. These two polymers were purified by repeated solution/precipitation in chloroform/methanol to remove unreacted initiators.

### Molecular Weight Determination

The molecular weight was determined by GPC with a Phendex 10<sup>4</sup> column calibrated with PSt standards, and with chloroform as eluent and Spectra Physics detector at 254nm.

### UV-VIS Spectra

UV-VIS spectra were recorded by Beckman DU-7 Spectrophotometer and HP 8542 Diode Array Spectrophotometer. The solvents tetrahydrofuran (THF), dichloromethane and chloroform were analytically pure reagents. The concentrations mentioned in the text are based on phenyl group.

## RESULTS AND DISCUSSION

### Polystyrene

Comparison of the UV spectra of PSt and its model compound ethylbenzene showed a shoulder at around 290nm for the former. (Fig. 1)

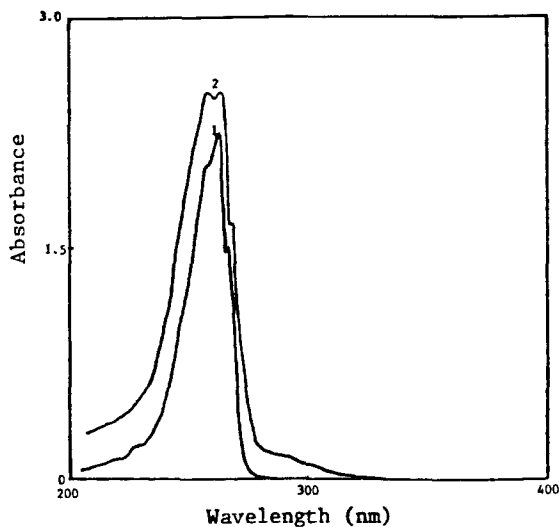


Fig. 1 Absorption spectra of  
1. ethylbenzene 2. PSt  
(in chloroform, concentrations are 10<sup>-2</sup>M)

New absorption bands are usually caused by charge-transfer interaction(8-11). Although no such interaction exists in PST, the structure contains phenyl groups separated by three carbon atoms. The PST chain is sufficiently flexible so that free rotation is possible about the carbon-carbon bond. Accordingly, one can expect an interaction between phenyl groups, which may bring about new absorption at longer wavelengths. In ethylbenzene solution, the solute molecules are separated far away from each other, so that no associative interaction takes place, and no absorption at longer wavelength can be observed.

We prepared several PST samples with different molecular weights, however, their UV spectra were quite similar.

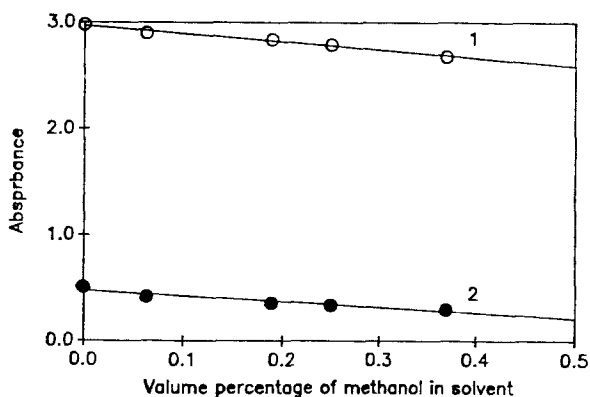


Fig. 2 Relationship between absorbance and THF/methanol ratio  
1. at 260nm, 2. at 295nm

Fig.2 shows the absorbance of PST in different mixed THF/methanol solutions. The absorbance at 260nm ( $A_{260}$ ) is due to isolated phenyl groups, while that at 295nm ( $A_{295}$ ) is most likely due to interaction between them. THF is a good solvent for PST, in which the PST chains are relatively extended, so the chromophores can absorb the light without much mutual interference. By adding methanol and increasing its concentration in the mixed solvent, the PST chains become closely tangled. the chromophores inside cannot absorb the light "normally" because of the "screen effect" of the outside chromophores, which leads to a decrease of both  $A_{260}$  and  $A_{295}$ .

If interaction between non-adjacent chromophores plays an essential role in the absorption at longer wavelengths, increasing amounts of methanol in the solvent would promote the interaction of non-adjacent phenyl groups to increase  $A_{295}$ . However, this does not happen. Therefore, associative interaction occurs essentially between neighboring phenyl groups.

## Polymers of Styrene Derivatives

The UV spectra of styrene derivatives shown in Fig. 3 provide further evidence for the interaction of pendant aromatic groups. Although at lower concentration, PSt shows absorption broadening above 280nm.

P $\alpha$ -MSt has an  $\alpha$ -methyl group and its absorption spectrum is very similar to PSt. Evidently the methyl group does not affect the interaction between phenyl rings.

P4-MSt has a methyl group on the phenyl ring which increases the electron density of the ring and consequently increases the interaction between them. A new absorption band is evident at 295nm.

The t-butyl group of Pt-BuSt is an even stronger electron-donating group than the methyl group. This polymer exhibits a strong absorption peak at 294nm.

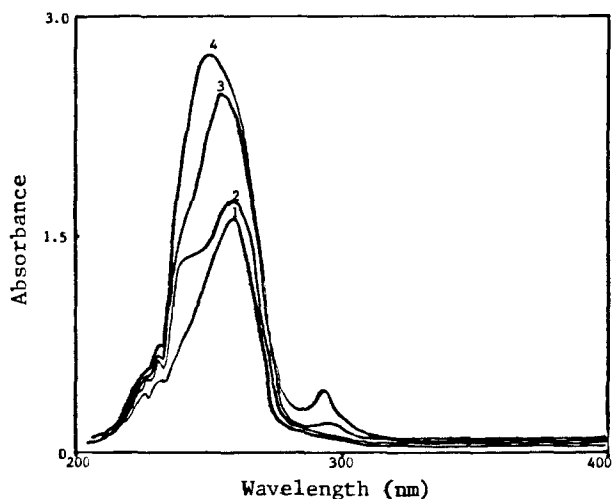


Fig. 3 UV absorption of polymers of styrene derivatives (in THF)

1. PSt ( $9.1 \times 10^4$ )
2. P $\alpha$ -MSt ( $1.1 \times 10^4$ )
3. P4-MSt ( $1.8 \times 10^5$ )
4. Pt-BuSt ( $1.8 \times 10^4$ )

## Interaction between PSt and TCNE

A large body of literature concerns charge-transfer interaction between polymers with electron-donating side groups and small molecule acceptors(12-16). The wavelengths of charge-transfer complex peaks and the equilibrium constants are quite different from that of CT complexes between small compounds.

The benzene ring is a very weak electron-donor; the interaction between PSt and acceptors was rarely studied. Evans (15) reported "donor-acceptor" complexes of PSt/iodine and PSt/silver perchlorate. It is known that benzene and its derivatives

can form charge-transfer complexes with tetracyanoethylene (TCNE), one of the strongest acceptors, so the CT complex formation may be expected for PSt/TCNE. Fig. 4 shows the UV-VIS spectra of ethylbenzene/TCNE, PSMMA/TCNE and PSt/TCNE systems. A new CT absorption peak appears with the first system, indicating strong charge-transfer interaction. The other two systems exhibit only an absorption shoulder, suggesting a weak interaction.

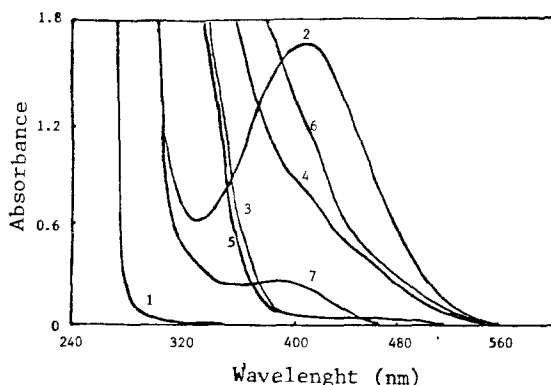


Fig. 4 UV-VIS spectra (in  $\text{CH}_2\text{Cl}_2$ )

1. ethylbenzene      2. ethylbenzene/TCNE
3. PSt              4. PSt/TCNE
5. PSMMA          6. PSMMA/TCNE
7. TCNE

( [donor] = 0.2M, [TCNE] = 0.04M, except for [ethylbenzene] = 0.04M in curve 2)

From the Benesi-Hildebrand equation(16)

$$1/\text{O.D.} = (1/K\epsilon_c b)(1/a) + 1/\epsilon_c b$$

the equilibrium constant  $K$  of CTC could be calculated, where O.D. and  $\epsilon_c$  represent absorbance and distinction coefficient of the CTC respectively,  $a$  and  $b$  refer to the concentrations of electron-donors and electron-acceptor, respectively. The  $K$  values were calculated to be 0.65, 0.52 and 0.44 for ethylbenzene/TCNE, PSt/TCNE and PSMMA/TCNE systems, respectively. Iwatsuki(12) reported a similarly higher  $K$  value for  $N,N$ -dimethyl-toluidine (DMT)/trinitrotoluene(TNT) than poly( $p$ - $N,N$ -dimethylaminostyrene) (PAST)/TNT. The larger entropy of polymeric donors was considered to be responsible for the lower  $K$  of their CT complexes. When the phenyl groups are separated by other groups (as in St/MMA copolymers) the  $K$  value would decrease further, which is also in agreement with previous investigations(12,13). It seems that the association between phenyl rings would promote their electron-donating ability.

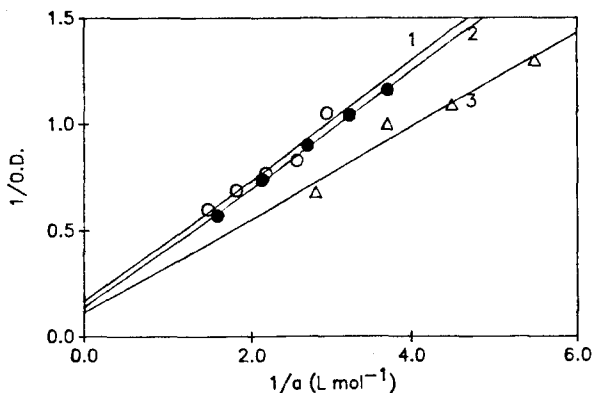


Fig. 5 Benesi-Hildebrand plots  
 1. ethylbenzene/TCNE 2. PSt/TCNE 3. PSMMA/TCNE

#### ACKNOWLEDGEMENT

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