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Thermal stability of conductive charge transfer complexes of poly(4-vinylpyridine)-poly(dimethylsiloxane) block copolymers

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Summary

Thermal stability of conductive charge transfer complexes of poly(4-vinylpyridine)-poly(dimethylsiloxane) (P4VP-PDMS) block copolymers with tetracyanoquinodimethane (TCNQ) was investigated by using thermal gravimetric analysis (TGA). The results show that both TCNQ simple and complex salts of polymers are thermally stable up to 800^{o}C and depending on the amount of added neutral TCNQ, the residual product increased up to 75%.

Introduction

Due to the great need for conductive, processable and flexible polymers (1), intensive studies on conductive properties of TCNQ doped poly(4-vinylpyridine) homopolymers (2,3) and its block copolymers (4-7) have been carried out. However, in spite of the obvious importance of polymer's stability in any potential applications of conducting polymers, there seems to be almost no report in the literature regarding thermal stability of these conductive composites.

In this paper, thermal stability of conductive charge transfer complexes of P4VP-PDMS block copolymers with TCNQ by using thermal gravimetric analysis has been reported.

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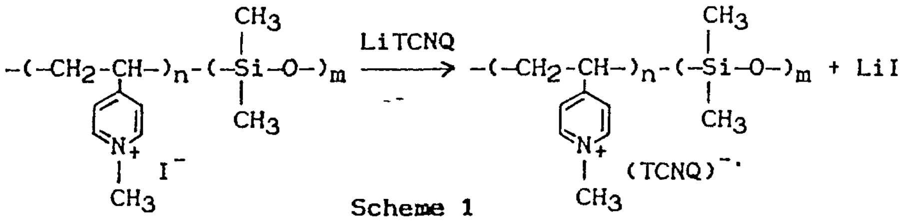
Experimental

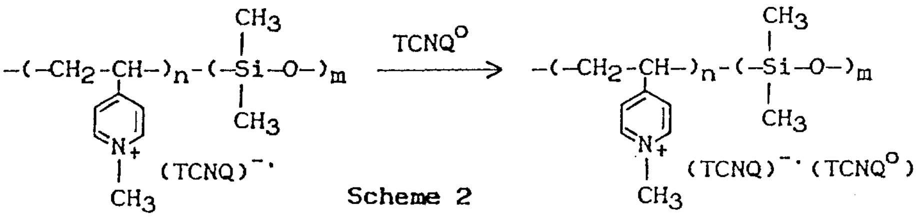
Block copolymers were synthesized by anionic polymerization technique with sodium naphthanate as initiator in THF/pyridine mixture at -70°C. The copolymer compositions were determined with Micro Kjeldahl nitrogen analysis and elemental analysis techniques. The block copolymer PVPS 1 was then completely quaternized with methyl iodide at 50°C (PVPSQ 1).
Charge transfer complexes of the polymer were prepared by the reaction of quaternized polymer and LiTCNQ (simple salt) (PVPSQD 1) and additional neutral TCNQ (complex salt) in 10% (PVPSQDC1 1), 17% (PVPSQDC2 1), 30% (PVPSQDC3 1) compositions. Details of polymerization, quaternization reactions (8) and preparation of charge transfer complexes (7) are the subjects of separate publications.
Conductivity of the samples were measured by four probe technique. Temperature stability of them were studied by Du Pont 951 TGA analyzer.

Results and Discussion

Schemes 1 and 2 show the preparation of polymeric simple and complex salts, respectively, from quaternized P4VP-PDMS block copolymers with methyl iodide.



Scheme 1



Scheme 2

The measured conductivities of these complexes are tabulated in Table 1.

Table 1 Conductivities of polymeric TCNQ simple salts

Sample	Composition (%P4VP)	Conductivity, σ ($S.cm^{-1}$)
PVPQD	98	$4.1*10^{-3}$
PVPSQD 5	93	$4.1*10^{-3}$
PVPSQD 2	84	$3.3*10^{-3}$
PVPSQD 1	71	$1.3*10^{-3}$
PVPSQD 4	64	$1.7*10^{-3}$
PVPSQD 3	58	$1.1*10^{-3}$

The conductivities of block copolymers as well as those of P4VP were in the order of 10^{-15} Scm^{-1}. After the quaternization of P4VP block in copolymers, conductivity values increased to 10^{-5} Scm^{-1}. It seems from the Table 1 that conductivities of simple salts are not much affected from the existence of insulating PDMS block in the copolymers. This is an expected result, since all block copolymers show a continuous P4VP phase resulting in greater number of charge carriers per unit volume in major component for electron transport (9).

The effect of $TCNQ^{o}$ content on the conductivity of the PVPSQD 1 sample are given in Fig.1. As the content of neutral TCNQ is raised, conductivity increase with a maximum at about 30% $TCNQ^{o}$ doping, and then decreases, suggesting that in the complex salt there is an optimum amount of $TCNQ^{o}$ where the conductivity is the highest.

Thermal stabilities of TCNQ complex salts of P4VP-PDMS block copolymer with 71 % P4VP content and related compounds followed by TGA are interpreted in Fig.s 2-4.

Fig.2 shows thermograms of block copolymer and its quaternized form in nitrogen atmosphere. For PVPS 1, a small weight loss was observed between 25°C and 350°C whereas beyond

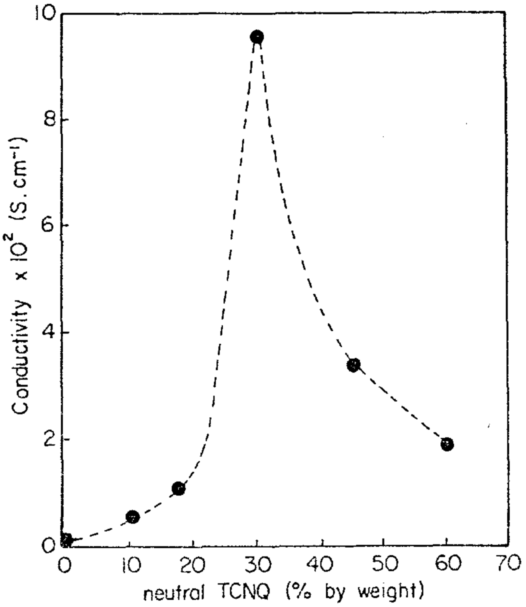


Fig.1 Effect of $TCNQ^o$ on conductivity of polymeric simple salts

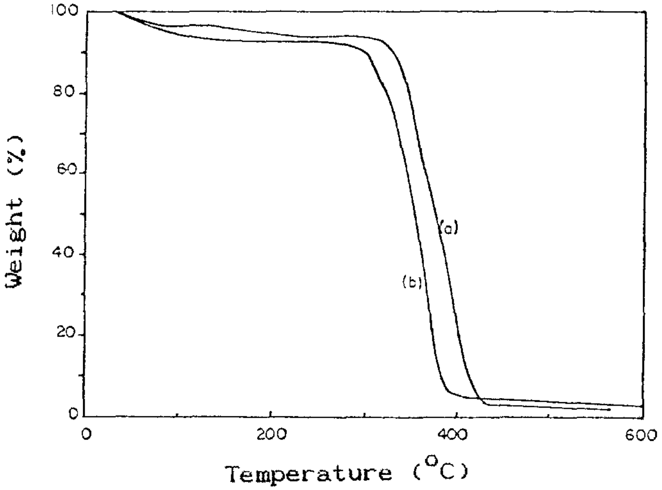
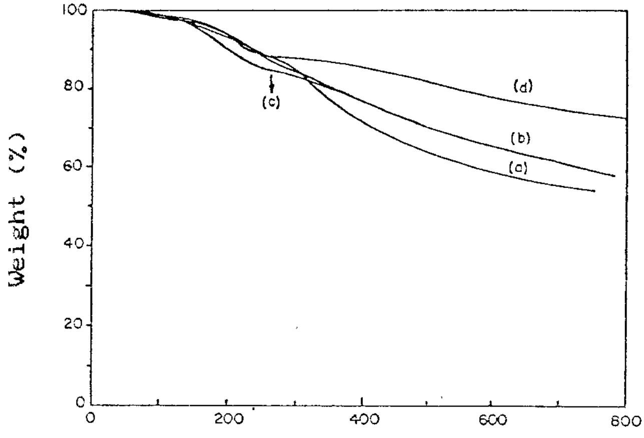


Fig.2 Thermograms of (a) PVPS 1,(b) PVPSQ 1 samples in nitrogen atmosphere

that temperature a large weight loss occurred. This shows that the sample is thermally stable up to 350°C (curve a). Degradation of quaternized form of this block copolymer (curve b) in small amounts starts between 100-150°C with the elimination of methyl iodide as reported by Karasz et al. (4) whereas occurrence of large weight loss showed a shift to lower temperatures.

The TCNQ simple and complex salts of this polymer exhibited different degradation kinetics as can be seen in Fig.3.



Temperature (°C)

Fig.3 Thermograms of (a) PVPSQD 1, (b) PVPSQDC1 1, (c) PVPSQDC2 1 and (d) PVPSQDC3 1 samples in nitrogen atmosphere

In the simple salt thermogram (a), an additional small weight loss around 250-300°C which can be attributed to TCNQ desorption was observed (TCNQ in its pure state sublimes around 275°C)(4) and at about 800°C almost 52% of sample stays as residual compound. In the complex salts thermograms (b,c,d), the increase in the amount of added TCNQ° caused an increase in the amount of complex salt formed and displaces the TGA curve to higher temperatures. Also, amount of residual product after 800°C was found to increase up to 75% as the TCNQ° content increases in the sample. This result shows that the complex salts are thermally more stable than simple salt.

In the presence of oxygen, thermogram of complex salt having 10% neutral TCNQ is given in Fig.4.

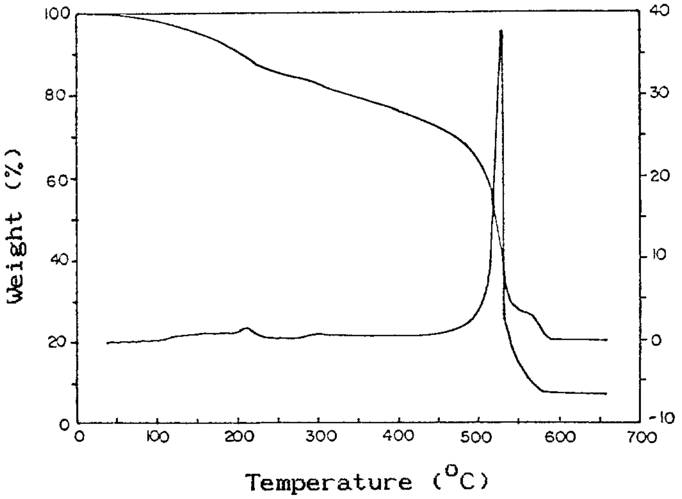


Fig.4 Thermogram of PVPSQDC1 1 sample in oxygen atmosphere

A heat resistance up to about 500°C then a rapid degradation is evident with 20% residual product. It is reported (10) that, at temperature above 150°C in air, polysiloxanes show gradual crosslinking through siloxane bridge leading a heat resistance up to 250°C. So, this rapid weight loss around 550°C may be attributed mainly to the oxidative degradation of modified P4VP segments.

Table 2 gives the temperatures at which 10, 20, 40, 50, 75 %

Table 2 Thermal characteristics of charge transfer complexes of P4VP-PDMS block copolymer

Sample	% Decomposition				
	10	20	40	50	75
PVPS 1	322	335	370	375	375
PVPSQ 1	210	335	510	520	530
PVPSQD 1	200	350	705	-	-
PVPSQDC1 1	220	330	550	-	-
PVPSQDC2 1	215	320	625	-	-
PVPSQDC3 1	250	550	-	-	-

decompositions take place. In all TCNQ simple and complex salts, it was observed that below 550°C the decomposition is not more than 40 % at most. In some samples, the decomposition up to 550°C is only about 20%. The complex salt PVPSQDC3 1 having 30% neutral TCNQ is found to be thermally most stable. A two step degradation was observed in simple and complex TCNQ salts. Activation energies for thermal decomposition of these polymers were calculated for the first and second transitions by the method of Broido (11) (Table 3). This method is based on the following equation ;

$$\ln[\ln(1/y)] = -(E/R)(1/T) + \text{constant}$$

where y: fraction of the number of initial molecules not yet decomposed
T: absolute temperature
E: energy of activation
R: the gas constant

Table 3 Energy of activation (kj) for degradation of charge transfer complexes of P4VP-PDMS block copolymer

Sample	1st transition	2nd transition
PVPS 1	-	99.2
PVPSQ 1	-	17.2
PVPSQD 1	17.6	10.9
PVPSQDC1 1	14.2	21.8
PVPSQDC2 1	15.5	15.9
PVPSQDC3 1	21.7	5.9

According to this equation, the values of ln [ln(1/y)] are plotted versus 1/T with a slope of (E/R). Activation energies tabulated in Table 3 varied widely. The maximum values for the first and second transitions were found to be 21.7 kj and 99.2 kj, respectively, by this method.

Conclusions

Charge transfer complexes of P4VP-PDMS block copolymers with TCNQ were found to be thermally stable up to 800°C with a residual product of only 75%.
High thermal stability in addition to the conductivity (10^{-2} Scm^{-1}) and processability makes these charge transfer complexes promising for commercially interesting applications.

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