Macromol. Symp. ***2001,*** *166, 189-194*

Thermoreversible polyaniline gels

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SUMMARY: Polyaniline (PANI) forms thermoreversible gels in different sulphonic acids e.g. dinonyl napthalene sulphonic acid (DNNSA), dinonylnapthalene disulphonic acid (DNNDSA), ± camphor – 10 – sulphonic acid (CSA) and dodecyl sulphonic acid (DSA) when processed from the formic acid medium. The surfactant concentration has been varied from weight fraction of PANI (W_{PANI}) = 0.05 – 0.60. In most cases at W_{PANI} = 0.05 – 0.40 compositions fibrillar network structures are observed from SEM study. They also exhibit reversible first order phase transition during both heating and cooling in DSC. The melting temperature and the gelation temperature increases with increase in surfactant concentration of the gel. From the WAXS pattern it is concluded that crystallization of the surfactant tails anchored from the nitrogen atom of PANI through its SO_3 H head group is responsible for gelation. The conductivity of all the gels with increase in PANI concentration showed a maximum with composition. The maximum conductivity is ~0.01 S/cm, for W_{PANI} = 0.22. The conductivity variation has been explained by considering it as a function of both interchain and intrachain contributions.

Introduction:

Thermoreversible gels of polymers are extensively studied for the past few years[1-3]. The gels reported are polymer – solvent type gel, where the polymer dissolved in a solvent at high temperature becomes gel on cooling and reverses to sol on heating. Very recently, a new type of thermoreversible gel is reported, where there is no solvent but some surfactants are present to produce the gel, and these may be referred as polymer – surfactant type gel[4-5]. Polyaniline (PANI) is an important conducting polymer but it is insoluble and infusible, so it is difficult to process[6]. Attempt has been made to produce thermoreversible gels of this polymer using a number of sulphonic acids e.g.- dodecyl benzene sulphonic acid (DBSA)[4], dinonyl napthyl sulphonic acid (DNNSA), dinonyl napthyl di sulphonic acid (DNNDSA), (±) – camphor – 10-sulphonic acid (CSA) and dodecyl sulphonic acid (DSA)[5]. 15% (w/w) PANI with the above surfactants have been found to produce thermoreversible gels when they are made from formic acid medium. Here, we shall report the gelation behavior of PANI with a surfactant for the whole composition range.

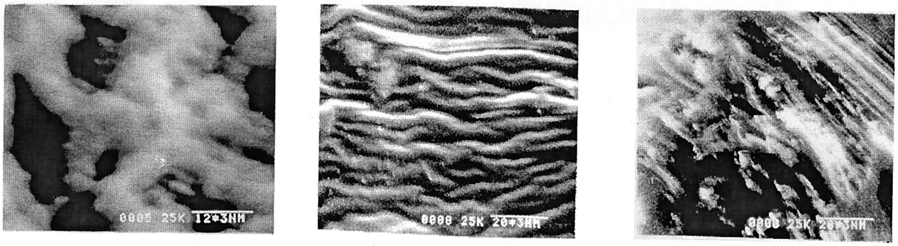
CCC 1022-1360/00/$ 17.50+.50/0

Experimental:

Polyaniline (PANI) was prepared in the laboratory by polymerizing aniline in hydrochloric acid medium with ammonium persulphate as initiator$^{6)}$. It was converted to emeraldine base form (EB) by treatment with NH_4OH solution. The sample had molecular weight $(\overline{M}_v) = 15{,}000$. Dopant DNNSA was kindly donated by Dr. P. J. Kinlen of Mansanto Company, St. Louis, U. S. A.$^{7)}$. It was a commercial product of King Industries and had a commercial name Nacura – 1051. It was supplied in diluted condition with 50% ethylene glycol butyl ether. The diluent concentration was taken into account during the blend preparation. PANI (EB), and DNNSA in different weight ratios were taken in formic acid medium (total concentration 2.5 weight %) and stirred at 65°C for 24 hours. Then the mixture was poured into a petridish and evaporated to dryness in a pool of air. Finally they were dried in vacuum at 60°C for one week$^{4)}$. By FTIR studies of these dried samples the absence of peaks corresponding to formic acid and ethylene glycol butyl ether were noted$^{5)}$. The SEM, thermal, WAXS and conductivity studies were made according to the procedure described earlier$^{5)}$.

Results:

In figure 1(a) – (c) SEM pictures of PANI – DNNSA system for $W_{PANI} = 0.05$, 0.4 and 0.6 are shown. So it is apparent from figure that the former two have fribrillar network structure while the later has not. So the fibrillar network structure is present for $W_{PANI} = 0.05 – 0.40$, but it is not observed for $W_{PANI} = 0.60$. It, therefore, indicates that PANI produces thermoreversible gel only in the composition range $W_{PANI} = 0.05 – 0.40$.



(a) (b) (c)

Figure – 1
SEM micrographs for PANI – DNNSA gel; (a) $W_{PANI} = 0.05$, (b) $W_{PANI} = 0.40$, (c) $W_{PANI} = 0.60$.

The presence of crystallites in the gel is confirmed from the WAXS pattern (figure - 2) where small peaks are present. The peaks are different from that of the PANI (EB) form and may be some new crystallites are produced due to doping with DNNSA. The electron diffraction pattern confirms the polycrystalline nature of the crystallites present in the gel.

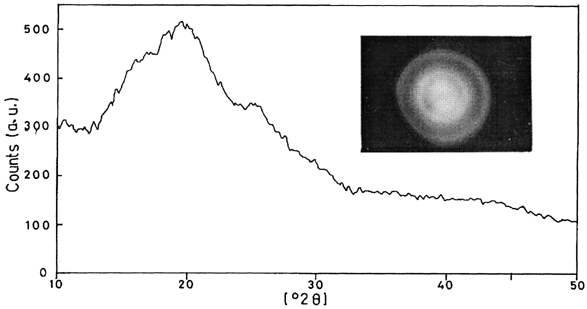


Figure – 2
WAXS pattern of PANI – DNNSA gel ($W_{PANI} = 0.40$).
[Inset – electron diffraction pattern]

The thermoreversible gels usually show first order phase transition$^{2)}$. In figure – 3, the DSC thermogramms of $W_{PANI} = 0.40$ for the first heating of the as prepared gel from – 20°C to 160°C, cooling from the melt and second heating after cooling to – 20°C are shown. It is apparent from the figures that there are two melting peaks fused together during first heating and second heating and it is also true for the cooling process.

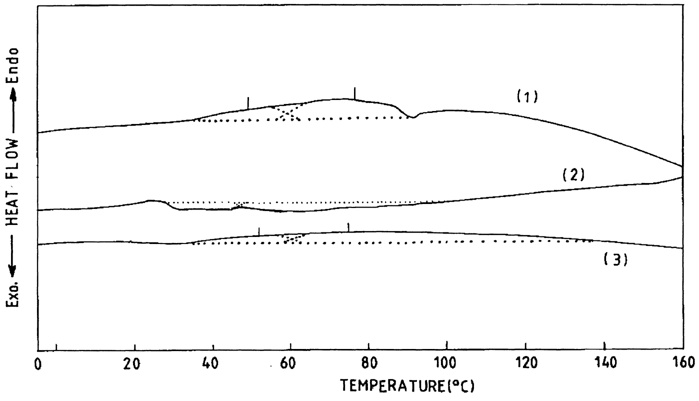


Figure – 3
DSC thermogramms of $W_{PANI} = 0.40$ in PANI – DNNSA gel.
(1) for first heating @ 10°C / minute (2) for cooling from the melt @ 5°C / minute (3) for the second run.

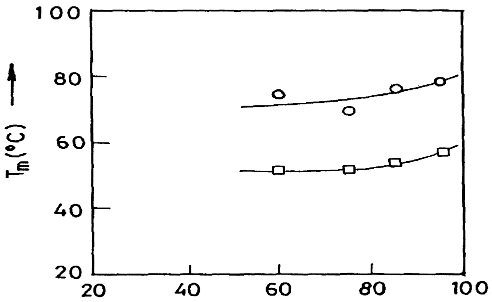


Figure – 4
T_m vs W_{DNNSA} plot for second heating in DSC for PANI – DNNSA

In figure – 4 the T_m for the second heating process are plotted with weight fraction of DNNSA (W_{DNNSA}). From the plot it is apparent that with increase in W_{DNNSA} concentration in the gel melting points of both the peaks increases. This is true for other systems also. The ΔH values also increase with increase in W_{DNNSA} in the gels. The occurrence of two peaks in polymer – solvent gels have been attributed to the polymer – solvent complex formation[8-10)]. However, in these gels no solvent is present. So to explain this phenomenon we want to consider the lamellar model for the polymer – surfactant type gel[5)]. According to this model the surfactant molecules become anchored with the nitrogen atoms of PANI and they become elongated[11-12)]. This produces both monolayer and bilayer of the surfactant tails[5)]. This ordered arrangements crystallize to produce the gel. In this model we, therefore, expect that two different type of crystallites to be formed during gelation the monolayer forms the lower melting zone and the bilayer produces higher melting zone because of higher density in this zone. The presence of two melting peaks or two exothermic peaks during cooling confirms the above viewpoint. Again both T_m's and the ΔH values decrease with decrease in W_{DNNSA}. This is because DNNSA under the anchored condition produce the crystallites, but not the PANI molecule and this makes PANI to behave as diluent, and so increasing concentration of PANI in the gel decreases the melting point and enthalpy[13)]. Therefore, the thermal data supports the lamellar model.

The conductivity values of the gels were measured using four probe method at 27°C[5)]. The conductivity shows a maximum at $W_{PANI} = 0.22$. The conductivity in this system is due to two-contribution (1) intrachain and (2) interchain due to crosslinking[14)]. The increase in conductivity with increase in sulphonic acid is first due to doping of PANI by sulphonic acid and with further increase this intrachain contribution increases. When network structure formation begins both intra and inter chain contribution takes place. With further increase in surfactant the conductivity decreases due to increase in concentration of nonconducting surfactant in the material.

Conclusion:

PANI – DNNSA system produces thermoreversible gel when processed from formic acid for the composition range $W_{PANI} = 0.05 - 0.40$. The X –ray and electron diffraction study confirms the presence of crystallites in the gel. The thermodynamic study confirms the presence of two types of crystallites in the gel. It has been explained from the lamellar model of polymer – surfactant type gel. The monolayer and the bilayer of surfactant tails form the different crystallites. The conductivity initially increases with increase in PANI (EB), shows a maximum at $W_{PANI} = 0.22$ and then decreases with increase in PANI (EB) concentration.

Acknowledgement:

We gratefully acknowledge Dr. P. J. Kinlen, Monsanto Company, U. S. A. for his valuable gift of DNNSA and CSIR (grant no. 01(1449)/97 EMR.11), New Delhi for financial support of the work.

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