

The Effect of Alkali Salt on Solvent-Polyacrylonitrile Interaction

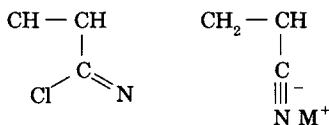
M. R. PADHYE and A. V. KARANDIKAR, *Centre of Advanced Studies, Department of Chemical Technology, Matunga, Bombay - 400019, India*

Synopsis

In solvent spinning of polyacrylonitrile from DMF or DMSO, it is observed that complete removal of solvent is rather difficult. It is shown that addition of Lithium salt, e.g., lithium bromide to the solution before casting a film helps in removing the solvent easily. The probable mechanism of the action of lithium salt in solvent removal is investigated, and it has been shown that the formation of coordinate linkage with the ion stops solvent bonding.

INTRODUCTION

A large amount of work has been done by Bamford and his co-workers on the effect of metal ions on radical polymerization both in aqueous and non-aqueous media. The results allow kinetic constants of radical salt reaction to be calculated. The effect of FeCl_2 on acrylonitrile polymerization in DMF was investigated, and the rate of initiation and chain termination reactions determined.¹ In a further study by Bamford² of effect of lithium chloride on polymerization reaction of acrylonitrile in DMF, it was observed that it has a pronounced effect and leads to an increase in the rate as well as degree of polymerization. This effect was explained as due to the fact that small fraction of radicals enter into complex formation with both types of ions derived from salt, namely, lithium chloride. To explain substantial increase in propagation coefficient, the authors envisage a complex formation of ions, with terminal nitrile group:



The discussion, as authors point out, have not taken into consideration any effect of complex formation, between acrylonitrile monomer itself and the ions of lithium salts. Since the conductivity of salt in DMF with and without acrylonitrile is the same and also since the salts are insoluble in pure acrylonitrile, the interaction between monomer and ions is ruled out. While explaining the effect of solvent on photopolymerization, it is observed that changes in the rate of propagation are controlled by complex formation of radical with salt, monomer or with metal salt particularly as observed in LiCl -methacrylate complexation.

Molecular complexes are important in the synthesis of completely new alternating copolymers of vinyl monomers by the use of Lewis acids like

ZnCl₂ or alkylammonium chlorides which exert a powerful directing effect in copolymer synthesis.³

The effect of metal salts on C≡N was recorded,⁴ and it was observed that C≡N frequency shows a long wavelength shift in case of radical ion salt, e.g., in TCNQ. The normal band at 4.5 μm shifts to 4.55–4.60 μm. On the other hand, nitrile frequency is found to shift to lower wavelength (higher frequency side) as a result of the complexing of the C≡N with Lewis acid. C≡N force constant increases upon coordination and is the main cause of frequency increase. This adduct formation probably involves N—lone pair electrons. The frequency of 2266 cm⁻¹ in CH₃CN in some adducts shifts to as much as 2278 cm⁻¹, depending on the Lewis acid.

There is, however, no data on the effect of metal salts and specially the lithium salt on the solvent release after the solution spinning or extrusion. Polyacrylonitrile is particularly interesting from the point of view because it is observed that the two common solvents DMF and DMSO are removed with difficulty from the polymer⁵ and more thorough prolonged treatments are necessary to get solvent free system. This investigation was undertaken to study the effect of LiBr on the process of solvent removal in solvent extruded films.

EXPERIMENTAL

Polyacrylonitrile (PAN) powder from Bayer, Germany was used for casting the films. Infrared spectra showed that it is a homopolymer. Dimethyl formamide (DMF) of spectral grade of SD Chemical Co. was used.

(i) PAN films were cast from 10% solution on a glass plate, and solvent was evaporated under an infrared lamp, taking care that the temperature does not exceed 85–90°C. The films were washed and stored in vacuum desiccator for 24 h. A second set of films was cast in same way except that 10% solution of lithium bromide in DMF was taken, into which 10% PAN was dissolved. The films were cast washed in cold water, and stored in a vacuum desiccator. Infrared spectra of all these films were studied.

(ii) Infrared spectra of acrylonitrile monomer with and without LiBr in solution was studied. The molar ratio of monomer:LiBr selected were varied in the range of 13:1, 11:3, 9:5, 1:1.

(iii) In order to study interaction between acrylonitrile monomer and LiBr, acrylonitrile solution in carbontetrachloride of 10*M* concentration was prepared. Similarly 1*M* LiBr solution in carbontetrachloride was prepared.

Finally, LiBr solution from stock was added to acrylonitrile stock solution in various proportions to vary the proportion of AN:LiBr. Infrared spectra of these solutions were recorded.

(iv) Infrared spectra of acrylonitrile monomer and solution of LiBr, KBr, LiCl, and NaCl in the monomer in various concentrations was studied to see the effect of change in the anion and the cation part of salt on the spectrum of the monomer.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) shows the infrared spectra of PAN films cast from DMF solution with and without LiBr. Both types of films were given iden-

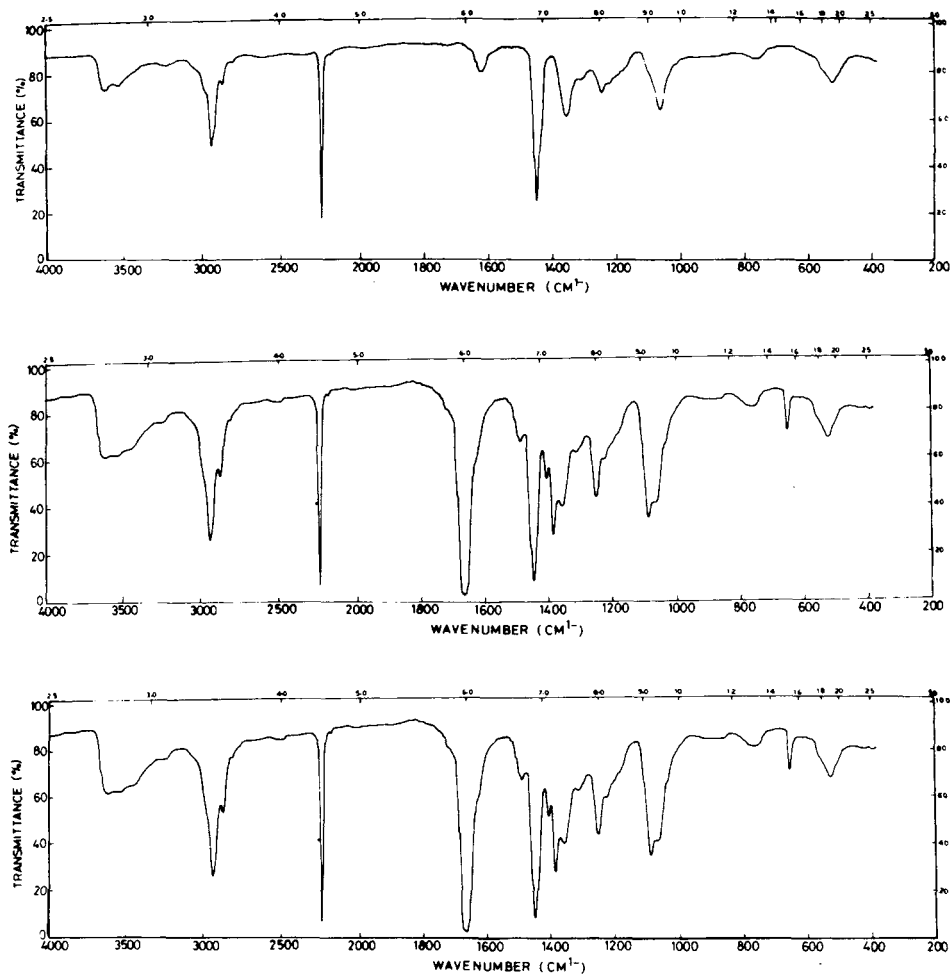


Fig. 1. (a) PAN film cast from DMF LiBr solution. (b) PAN film cast from DMF solution without LiBr. (c) PAN film cast from DMF solution with LiBr solvent was removed with vacuum evaporation; washing treatment was mitted.

tical after-treatment, and it is observed that when the film cast with LiBr are completely free of solvent and those without addition of LiBr still show residual DMF as seen from infrared spectra. Polyacrylonitrile is a polar polymer and is partly self-associated through interchain dipole-dipole interaction at the CN bands as also pointed out by Gupta and co-workers.⁶ They have also assigned the shifted $C\equiv N$ stretching vibration to the associated group band which they observed is present along with the normal $C\equiv N$ band. Solvent DMF breaks the self-association as it is a good solvent but is itself bound by dipole-dipole interaction at the nitrile groups. It would have seen necessary to stop this complexation to remove solvent completely. In Figure 1(c) is also recorded the spectrum of a film cast from DMF-LiBr solution, but the solvent was removed by vacuum evaporation of solvent. The washing treatment was omitted because it is during this that the lithium salt is washed out. This spectrum shows the extra band which is re-

moved when the same film is washed in water and before the spectra are recorded. This proves that some CN groups are complexed with LiBr added and become free when the salt is washed. That washing treatment removes the lithium salt completely was confirmed in two ways. First, the estimation of lithium salt in water washed film was estimated by atomic absorption and was about 1.96 ppm. Second, amount of lithium bromide liberated is estimated by determining the conductivity of water when a known weight of film is washed. It was observed that, by washing 0.18 g of film, 0.0254 g of LiBr out of 0.02650 gm of LiBr is liberated. From that LiBr still present in film is calculated which is 0.555 ppm.

Added lithium salt in the solution, since no solvent is retained, seems to stop PAN-DMF interaction, and the solvent is easily removed. The mode of action of LiBr in achieving this is illustrated by the succeeding work in solution phase planned specifically for this purpose.

In Figure 2 are given infrared spectra of DMF solution of acrylonitrile monomer with and without LiBr. It is observed that, in the solution phase in the presence of LiBr, in the $C\equiv N$ stretching region, in addition to a strong absorption at 2230 cm^{-1} assigned to a monomer, an additional band at 2249 cm^{-1} is observed. The latter band is absent in the spectrum of DMF solution. This shows a strong interaction of LiBr with $C\equiv N$ of acrylonitrile. Such a shift has already been noted when $C\equiv N$ is involved in coordination, viz., acrylonitrile liquid. The spectra of monomer with and without LiBr are given in Figure 3. It is observed that, in pure monomer, the nitrile

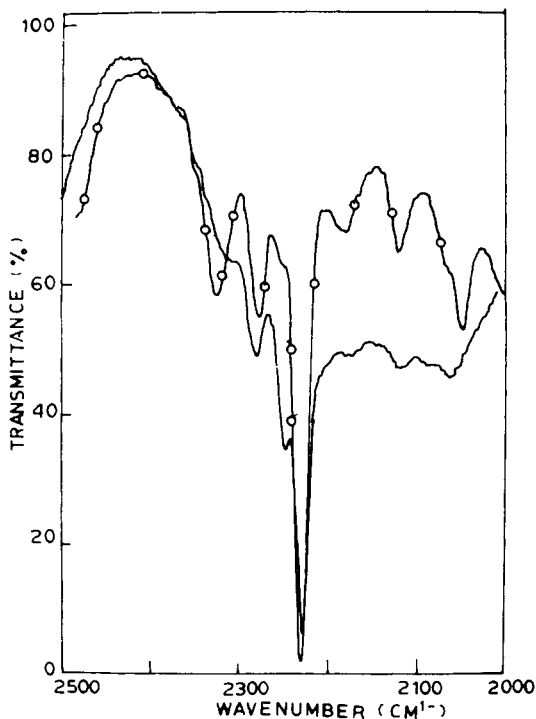


Fig. 2. Infrared spectra of DMF solution of acrylonitrile with (—) and without LiBr (—O—O—).

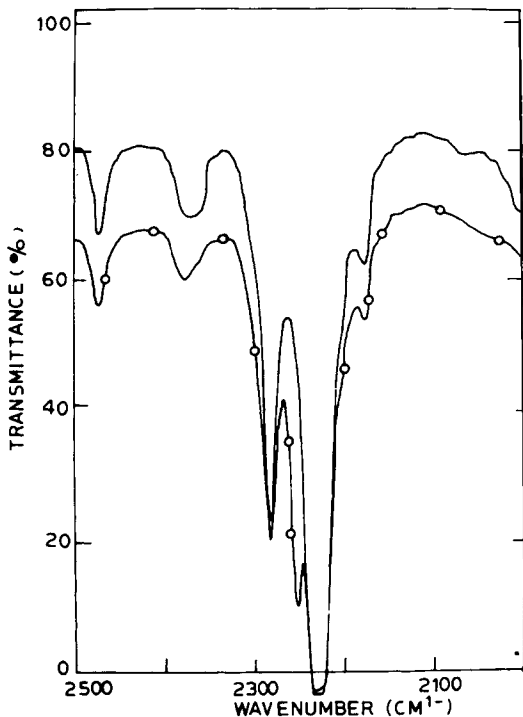


Fig. 3. Infrared spectra of acrylonitrile monomer with (-O-O-) and without LiBr (—).

forms a complex with LiBr, and the shifted band assigned to complexed $C\equiv N$ is observed. Acrylonitrile is a polar solvent and there is partial dissociation of LiBr in monomer, and thus complexation is possible, which is confirmed by conductivity. Measurement of conductivity of acrylonitrile monomer liquid (6.7×10^{-6} mho) and acrylonitrile liquid with LiBr (0.3×10^{-4} mho) shows the salt is dissociated in acrylonitrile solution. The system when taken in CCl_4 solution does not show any interaction as there is no change in acrylonitrile spectrum in the whole range of concentration of 0.1–10% by weight of LiBr added. This is shown in Figure 4; thus the effect of polar medium seems essential and thus confirms that the coordination complex is formed between Li^+ and the lone pair of electrons of nitrile nitrogen.

When other salts like KBr and NaCl were added to acrylonitrile monomer and spectra studied, though interaction was observed with LiBr, the other salts do not show shifted band or change in the nitrile region in infrared spectra. This pointed to the fact that it must be cation in LiBr, which is responsible for coordination band. It is proved by the study of the spectra of addition of LiCl in acrylonitrile monomer. Similar to LiBr it gives an additional band at 2249 cm^{-1} as seen in Figure 5.

According to El Sayed and Sheline⁷ the $C\equiv N$ frequency is decided by the relative contribution of $C\equiv N$ and $-C^+ = N^-$. The higher ionic contribution lowers the frequency and force constant. In the present case the observed increase in frequency in coordination can be understood. The donation of lone pair electron on nitrogen to Li^+ ion for coordination link-

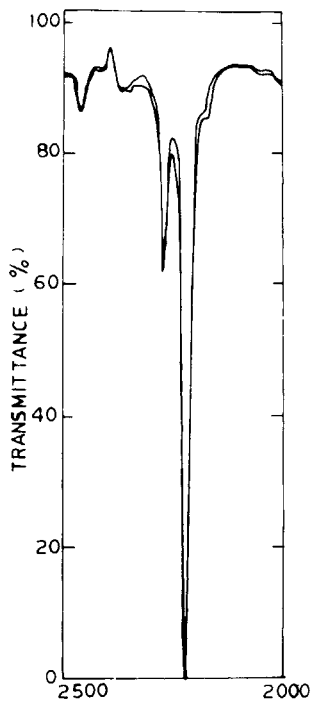


Fig. 4. Infrared spectra of CCl_4 solution of acrylonitrile monomer with various proportions of LiBr.

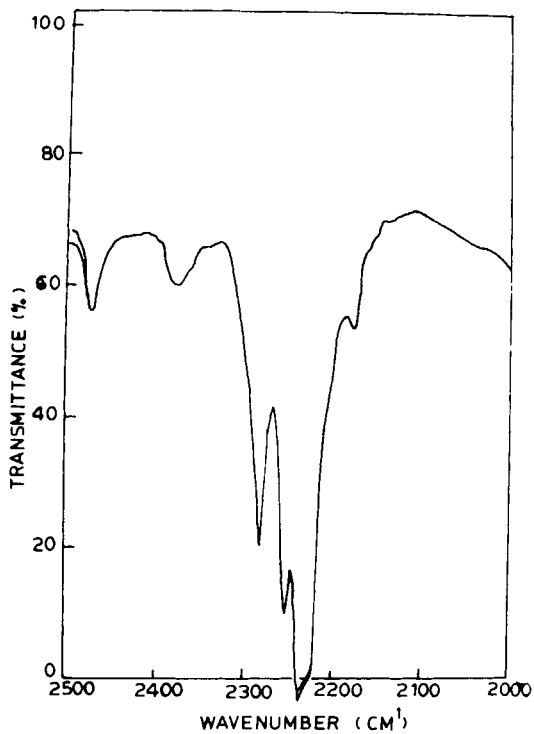


Fig. 5. Infrared spectra of acrylonitrile monomer with LiCl.

ages effectively increase the $C\equiv N$ bond strength by reducing the ionic character in $C\equiv N$ band. The frequency, hence, is expected to increase. For halogen attached to carbon as in $BrCN$ or ICN the frequency decreases. Frequency is also low in alkali metal cyanides KCN , $NaCN$, etc. due to contribution of $M^+—C=N^-$, but in the present case alkali metal attached to nitrogen side will act in opposite way and increase the frequency.

CONCLUSION

$LiBr$ plays an important role in PAN film cast from DMF solution. Lithium ions form a coordinate complex with CN group of PAN and thus prevent it from complexing with DMF, which in turn facilitates the removal of the solvent from the cast film.

References

1. C. H. Bamford, A. D. Jenkins, and R. Johnson, *Proc. Roy. Soc. A*, **239**, 214 (1957).
2. C. H. Bamford, *Proc. Roy. Soc. A*, **241**, 364 (1957).
3. M. Szwarc in *Molecular Behavior and Development of Polymeric Material*, A. Ledwith & A. M. North, Eds. Chapman & Hall, London, 1975.
4. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. M. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3375 (1962).
5. M. M. Coleman and R. J. Tetcavich, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 821 (1978).
6. A. K. Gupta and N. Chand, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1125, 1980.
7. El Sayed and Sheline, *J. Inorganic Nucl. Chem.*, **6**, 187 (1958).

Received January 18, 1984

Accepted June 18, 1984