An investigation of microstructure
of styrene-methacrylonitrile copolymers by FT-IR
spectroscopy

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Summary

The microstructure of styrene-methacrylonitrile copolymers has been investigated by FT-IR spectroscopy. The CN bond stretching frequency was shifted to a higher value with an increase in the methacrylonitrile (MAN) content in the copolymers. There was no linear relationship between the CN frequency and the diad fraction of MAN-MAN linkages in the copolymer chain, as reported previously for styrene-acrylonitrile copolymers. Different methods for the copolymer sample preparation can cause differences in the shifts in the CN frequency. This suggests that the polymer morphology plays an important role. A study of blends of poly(methacrylonitrile) (PMAN) with polystyrene has shown that the CN frequency is shifted to a higher value with an increase of the PMAN composition of the blends.

Introduction

Infrared (IR) spectra have been shown to be very useful for examining the compositional microstructure of copolymers (1-4). However, while the measurement of the properties of the monomer constituents in a copolymer using characteristic IR absorption bands is comparatively easy, and has been used widely for various copolymer systems, by comparison with the NMR technique, the analysis of the sequence distribution of monomer units which comprise a copolymer is often difficult and complex (5). Therefore, there have only been a small number of reports of the use of IR spectroscopy for sequence microstructure analysis for a limited number of copolymer systems (6-8).

In addition to providing information about the chemical structure of the component monomers which make up a copolymer, information about the distribution of the different units along the copolymer chain may be obtained from Fourier transform infrared (FT-IR) analysis in some suitable cases. The segments of a copolymer that differ in their sequence arrangement from that of the homopolymers should exhibit differences in the infrared spectra, resulting from changes in the interactions between neighbouring units (8). However, in most cases these differences are small and difficult to measure.

Early work on ethylene-propylene copolymers using infrared analysis was conducted by Drushel and co-workers (9). They assigned the four peaks in the methylene rocking region, at 813, 751, 731 and 722 cm^{-1}, to 1, 2, 3, and 4+ contiguous methylene groups, respectively. Similarly, they assigned the three peaks in the methyl rocking region at 937, 960 and 972 cm^{-1} to 1, 2 and 3+ contiguous methyl groups, respectively. They then illustrated the various arrangements of the ethylene and propylene repeat units within the

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copolymer structure which would result in these specific contiguous methyl and methylene groups.

There have also been reports on the effects of sequence distributions in the IR spectra of styrene-acrylonitrile (SAN) copolymers, using FT-IR. Koenig *et al.* assigned the different peaks in IR spectra, and correlated the frequency shifts and peak intensity changes with the SAN copolymer sequence distribution (10). Oi *et al.* found, by analysis of the IR spectra in DMF solution (5), that there was a linear relationship between the stretching frequencies of the nitrile group and the probability for finding an AN-AN diad in the SAN copolymer chain.

In this study, the infrared spectra for a series of random styrene-methacrylonitrile (SMAN) copolymers with various compositions will be analyzed to determine the dependence of the frequencies of the individual spectral peaks on the copolymer composition. In particular, the vibration frequencies for the nitrile group will be discussed in detail. Correlations will be established to relate changes in the peak positions to changes in the copolymer composition and monomer sequence distribution. In addition, the vibration band frequencies for blends of poly(methacrylonitrile) (PMAN) and polystyrene (PS) will be examined in order to compare the effects of inter- and intra-chain interactions on these bands.

Experimental Section

Materials. Synthesis and characterization of the SMAN copolymers were reported previously (16).

Sample Preparation. Three methods were used to prepare samples of the SMAN copolymers for IR analysis. (a) Solution Samples — The polymers were dissolved in dichloromethane at a concentration of 50 mg/mL, and the FT-IR measurements were made in a KBr sample cell of 2 mm path length. (b) KBr-Disk Sample — The polymers were dissolved in dichloromethane at a concentration of 5 mg/mL, and then precipitated into tenfold excess of methanol. The samples were washed and dried at 70^{0}C for 48 hours under vacuum. The sample and KBr powder were mixed (1:10 wt.) and milled, and then mould into a disk of 1 mm thickness. (c) Cast-Film Samples — The polymers were solvent cast from dichloromethane on to a teflon plate and allowed to dry for 12 hours at room temperature. Any residual solvent was then removed under vacuum. The thickness was controlled to be about 0.1 mm.

The PMAN/PS blend samples were prepared by the following procedure. Weighted quantities of PMAN and PS were dissolved in pyridine (10 mg/mL) and then precipitated into a tenfold excess of methanol. The samples were washed and dried at 70^{0}C for 48 hours under vacuum. The sample and KBr powder were mixed (1:10 wt.) and milled, and then moulded into a disk of 1 mm thickness.

FT-IR Measurement. The infrared spectra were recorded on a Perkin-Elmer 1700 Fourier transform infrared spectrometer operating in the 450 to 4000 cm^{-1} region. The spectra were acquired with 0.5 cm^{-1} resolution, 256 scans being accumulated in each case.

Results and Discussion

The molecular structure of the copolymers can be examined from their FT-IR spectra. A typical FT-IR spectrum is
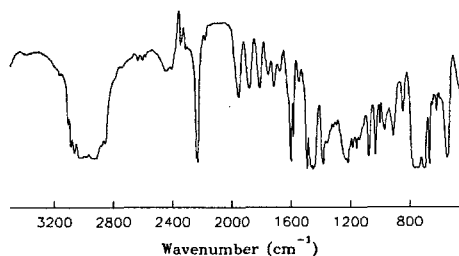

Figure 1. IR spectrum of SMAN copolymer with $Y_M=0.651$.

shown in Figure 1 for a copolymer KBr-disk sample, in which the methacrylonitrile (MAN) mole fraction, Y_M, is 0.651.

The infrared spectra of SMAN copolymers of various compositions were first analyzed to determine the relationship between the peak position and the copolymer composition. It was found that a number of peaks shift to higher frequencies as the amount of methacrylonitrile in the copolymer is increased. Figure 2 shows the relationship for six different spectral peaks for the SMAN copolymers. These peaks have been assigned in Table 1 (10,15).
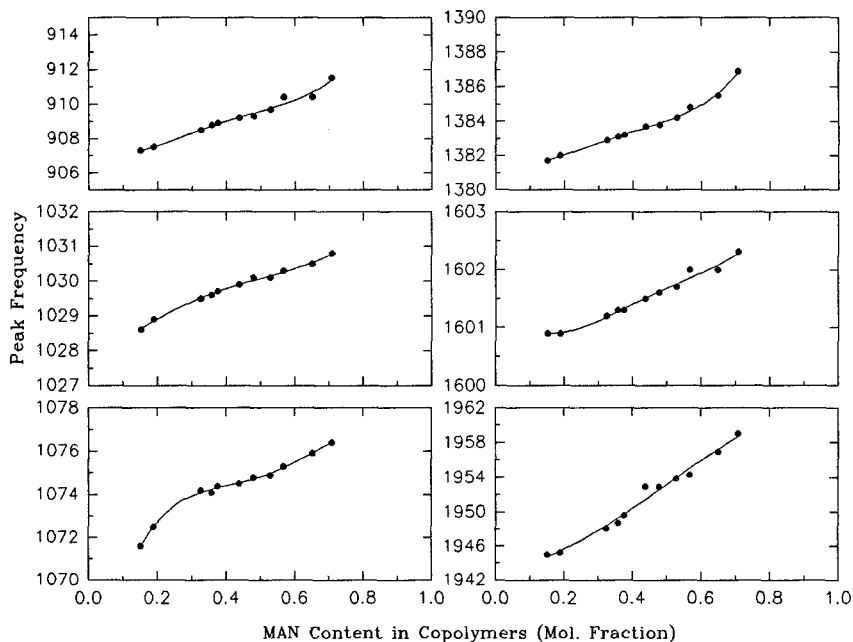

Figure 2. Plots of the frequency *versus* the copolymer composition for the various IR peaks.

Table 1. Assignments of six IR spectral peaks in SMAN copolymers

Frequency (cm^{-1})	Assignment
907.3	aliphatic CH wag band
1028.6	phenyl ring in-plane C-H bending vibration band (I)
1071.6	phenyl ring in-plane C-H bending vibration band (II)
1381.7	symmetric CH_3 umbrella deformation vibration band
1600.9	quadrant stretching of the phenyl ring C=C band
1945.0	phenyl ring combination or overtone band

* The peaks are identified by their frequencies in the spectrum of the sample with a MAN mole fraction of 0.152.

An important characteristic of PMAN and its copolymers is the presence of the strongly polar nitrile groups. The nitrile groups can interact with their surroundings in a variety of ways. These different interactions between the nitrile groups and their surroundings may lead to a change in the stretching frequency of the CN bond. Therefore, the stretching frequency of the CN bond may provide information about the microstructure of the SMAN copolymers, providing next neighbour effects are dominant.

The peak located at 2229.7 cm^{-1}, which is the CN bond stretching band for a SMAN copolymer with $Y_M = 0.189$, shifts to higher frequency with increasing methacrylonitrile content in the SMAN copolymers, as shown in Figure 3.

The high dipole moment (3.9 Debye) for the nitrile group can give rise to either a strong attraction or a strong repulsion (according to orientation) with similar groups or other substituents in a copolymer which possess a high dipole moment (11). The intra and inter molecular forces in a PMAN polymer

Figure 3. The shift of CN frequency of SMAN copolymers in KBr-disk (Y_M: 0.189, 0.376, 0.480, 0.651, 0.798, 1.000, from right to left).

chain result predominantly from these types of dipolar interactions (12,13). The adjacent nitrile groups in PMAN repel one another and force the polymer chain to adopt a conformation in which these repulsive forces are minimized. But nitrile groups on adjacent chains may be involved in attractive interactions. The incorporation of styrene units into a PMAN chain will reduce the extent of the repulsive interactions of neighbouring nitrile groups and will enhance the mobility of the polymer chain segments, thus allowing more attractive interactions to occur between the polar nitrile groups, as well as other groups in the copolymers.

At low concentrations of nitrile groups in a SMAN copolymer, the frequency of the CN resonance lies in the range of 2230 to 2231 cm^{-1}, depending on the nature of the matrix of the polymer (eg. solution or solid states). Thus, as the CN content of the polymer increases, the probability for the occurrence of adjacent MAN-MAN diad sequences rises, and hence the extent of repulsion between these neighbouring groups also rises. As the concentration of MAN units in the copolymer increases, so does the vibrational frequency of the CN bond, as shown in Figure 4.
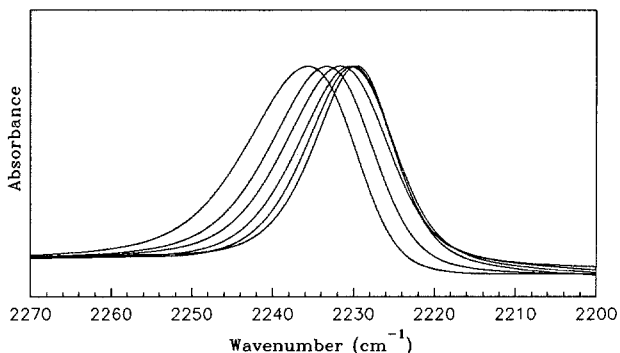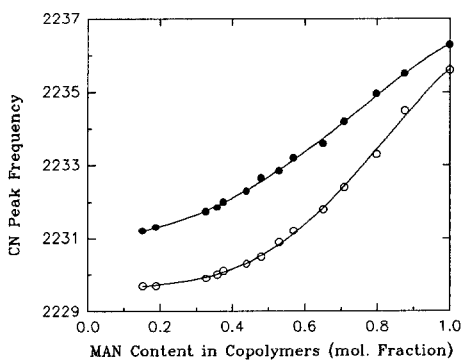

Figure 4. Relationship between the CN frequency and the copolymer composition (• solution sample; ○ KBr-disk sample).

The increasing vibrational frequency with increasing MAN content in the copolymers is consistent with an apparently higher force constant for the CN bond. This can be rationalized in terms of the repulsive forces which exist between the carbon and nitrogen atoms of neighbouring nitrile residues along the polymer chain, and which restrict the vibration of the two atoms in each of the nitrile groups.

Figure 4 shows the relationship between the CN bond stretching frequency and MAN content in the copolymers for the solution samples and solid state samples in the form of KBr-disks.

From Figure 4, the samples determined in dichloromethane solution have a higher stretching frequency for the CN bond than the corresponding solid state samples determined in the KBr-disk form. This may be attributed to the nature of the interaction between the copolymer chains and the dichloromethane solvent. The polar dichloromethane, which has a dielectric constant of 9.7, will interact strongly with the polar CN bonds in the copolymers, leading to an increase in the polarization of these bonds, and thus to a shift on their stretching frequency towards higher values.

Oi *et al.* have reported a study of styrene-acrylonitrile (SAN) copolymers in DMF solution by IR spectroscopy (5). According to their research, the positions of the CN bond stretching frequency were controlled by the sequence distribution of acrylonitrile (AN) units. The shift of the CN bond stretching frequency was found to vary in a linear manner with the probability of AN-AN linkages in the copolymers, P_{AA}. This indicated that the dominant interaction of the nitrile groups in SAN copolymers in DMF solution was the repulsion between the nitrile groups of the adjacent AN-AN units in the copolymer chain.

According to Oi *et al.*'s, the CN bond absorption frequency can be expressed by the equation:

$$\nu_{CN} = a P_{AA} + b P_{AS} \qquad (1)$$

where ν_{CN} is the stretching frequency of the CN bond in the copolymers, P_{AA} and P_{AS} are the diad fractions of AN-AN and AN-S linkages in the copolymers, respectively, and a and b are constants.

Since,

$$P_{AA} + P_{AS} = 1 \qquad (2)$$

From equations (1) and (2),

$$\nu_{CN} = b + (a - b) P_{AA} \qquad (3)$$

Therefore, according to equation (3), a plot of ν_{CN} *versus* P_{AA} should be a linear relationship.

In a previous report (16) the sequence distributions in the SMAN copolymers were examined. Accordingly, the diad fraction of MAN-MAN sequences in the copolymers, P_{MM}, can be calculated. The frequency of the CN band has been correlated with P_{MM} in Figure 5 for SMAN copolymers in solution and in the solid state. The plots in Figure 5 are distinctly curved, and thus do not fit the linear relationship proposed by Oi *et al.*, either in solution or in the solid state. This suggests that, while next neighbour effects play an important role in determining the CN bond frequency in the SMAN copolymers, these effects are not the only interactions which are important in these copolymers.

In addition to next neighbour interactions, the CN groups may also interact strongly with other distant CN groups along the polymer chain or with CN groups on

adjacent chains. In order to examine further the interactions of the nitrile groups in the copolymers, the FT-IR spectra of blends of PMAN and PS of different compositions have been studied. If the frequency of the CN bond stretch was dependent only on next neighbour interactions, the frequency of the absorption in the IR spectra of these blends should remain constant over the composition range for the blends. However, when the PMAN contents of the blends was increased, the CN bond stretching frequency was observed to shift to higher values. Figure 6 shows the relationship between the measured values of the CN bond stretching frequency and the corresponding PMAN content in the blend system. This figure clearly indicates that the positions of the CN bond stretching frequency in a PMAN-PS blend system shifts gradually to higher frequency as the PMAN content increases. Thus, the increase in the CN bond stretching frequency observed in Figure 4 results not only from the interactions of adjacent MAN-MAN units in the polymer chain, but also from the intermolecular interactions of MAN units. Comparing the frequency shifts of the blend samples (Figure 6) with the corresponding values for the solid state copolymer samples (KBr-disk) (Figure 4), we can conclude that in the solid state a contribution of about 20% of the shift in the CN bond stretching frequency comes from the intermolecular interactions of nitrile groups.

Figure 5. The CN frequency related to P_{MM} (• solution sample; ○ KBr-disk sample).
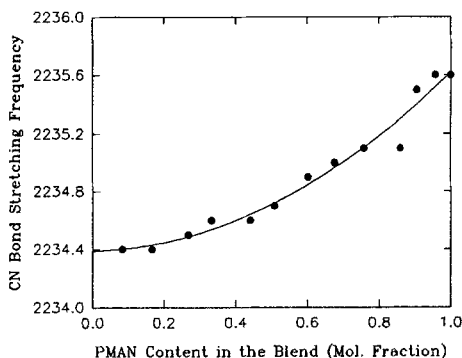
Figure 6. Relationship between the CN frequency and PMAN/PS blend composition.

It has been reported by Koenig *et al.* that the CN bond stretching frequencies were unaffected by changes in the SAN copolymer composition when the contents of acrylonitrile monomer in the copolymers were lower than 24.4 wt.% (38.8 mol.%) (10). They deduced that the nitrile groups are spectroscopically insensitive to changes in their environment below this composition, which they suggested was a result of the force constant of a triple bond being much larger than that for a single bond. However, in the SMAN copolymer system, either in solid state KBr-disk samples or in the solution samples, experimental results similar to those reported by Koenig *et al.* for the SAN copolymers could not be reproduced.

In the solid state, the molecular conformation and morphology of the SMAN copolymers will play an important role in determining the effect on the CN bond stretching frequency. The samples of SMAN copolymers prepared by solution casting have been examined to determine the effect of morphology on the CN bond stretching frequencies. Figure 7 shows the relationship between the CN bond stretching frequencies
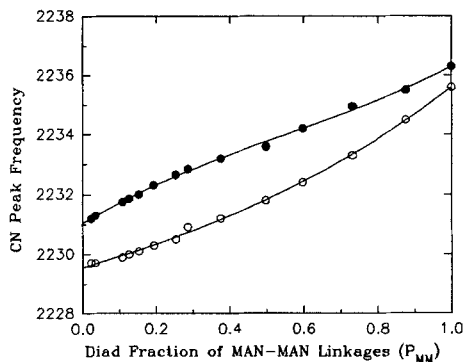
and MAN contents for these samples. During the preparation process for these samples, the solvent was slowly evaporated, so that the molecular chains will tend to achieve their equilibrium conformation. When molecular chains achieve their equilibrium conformation, the Gibbs free energy will be minimized.

For the polymer samples containing polar nitrile groups, the energy involved in the interaction of two nitrile groups can be given by (14):

Figure 7. Relationship between the CN frequency and copolymer composition for the cast-film samples.

(1) Antiparallel alignment

$$R{-}C{-}N$$
$$N{-}C{-}R$$

$$E{\uparrow}{\downarrow} = -\frac{\mu^2}{r^3} \qquad (4)$$

where μ is CN bond dipole moment and r is distance between two nitrile groups.

(2) Parallel alignment

$$R{-}C{-}N$$
$$R{-}C{-}N$$

$$E{\uparrow}{\uparrow} = \frac{\mu^2}{r^3} \qquad (5)$$

Therefore, the equilibrium conformation of molecular chains containing nitrile groups will have a tendency to maximize the antiparallel alignment of the nitrile groups of interacting pairs, and the stretching frequency of CN bond will be decreased. By comparison, the rapid precipitation in a non-solvent tends to "quench in" the polymer chain conformation in the original solution, in which polymer-solvent interactions are significant.

Comparing Figure 7 with Figure 4, we find that, in the higher MAN content region, the stretching frequencies of the CN bonds for the film samples which were cast from solution by slow evaporation are lower than those for the corresponding KBr-disk samples, which were prepared by rapid precipitation from solution. The macromolecular chain conformations in the cast-film copolymer samples will have a lower potential energy, so that the extent of antiparallel interactions between chains having been maxmized. Since the nitrile groups in the molecules have a tendency towards an antiparallel alignment, the stretching frequency of the CN bond will shift to a lower value in the evaporated films compared with the corresponding frequencies for the KBr-disk samples.

From Figure 7 we find that when the MAN content in the copolymers is less than
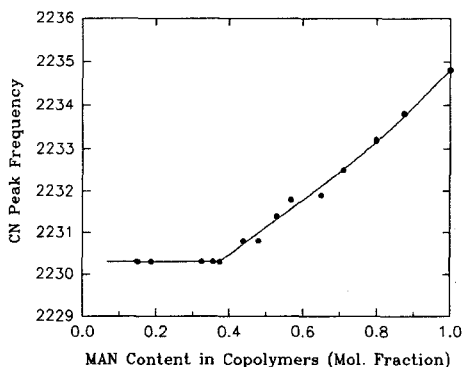
40 mol.% (30 wt.%), the stretching frequencies of the CN bond for cast-film samples were no longer effected by changes in the SMAN copolymer composition, as was reported by Koenig *et al.* for the SAN copolymers.

In the previous report we have examined the sequence distributions of MAN units in the SMAN copolymers by NMR spectroscopy (16). We have found that below an MAN composition of 40 mol.% the fraction of MAN sequences of length greater than two is very small. Thus, the MAN units in the copolymers in this composition range essentially all have at least one styrene neighbour. During the slow evaporation of the solvent, the copolymer chain is able to adopt a conformation which minimizes the repulsive interactions between adjacent groups and maximizes the attractive interactions between these groups. Thus, the results presented in Figure 7 suggest that there may be a specific interaction between the nitrile and styrene groups in the copolymers. In the region below 40 mol.% MAN content, this interaction would have the effect of making the CN bond stretching frequency independent of the MAN content in these copolymers. It has been shown that the results obtained from solid-state NMR support this suggestion (17).

When the MAN content of the copolymers is above 40 mol.%, some MAN units in the copolymer chain would not have an adjacent styrene unit. Then the repulsion between neighbour MAN units would lead to an increase in the CN bond stretching frequency. In addition, if the samples were dissolved in solution or if they were precipitated rapidly, as for the KBr-disk samples, the establishment of the equilibrium conformation to form a specific interaction between the methacrylonitrile units and their neighbouring styrene units would not be optimized. Therefore, the single, unique value for the CN bond stretching frequency would not be observed for the solution or precipitated samples when the MAN content in the SMAN copolymers is less than 40 mol.%.

References
1. Briber RM, Thomas EL (1985) Polymer, 26: 8
2. Doiuchi T, Yamaguchi H, Minoura Y (1981) Europ. Polym. J., 17: 961
3. Kawaguchi S, Kitano T (1991) Macromolecules, 24: 6030
4. Danusso F, Tanzi MC, Levi M, Martini A (1990) Polymer, 31: 1577
5. Oi N, Miyazaki K, Moriguchi K (1972) Kobunshi Kagaku, Eng. Ed., 1: 566
6. Schnell G (1966) Ber. Bunsenges. Physik. Chem., 70: 297
7. Yamashita Y (1967) Kagaku Zokan, 27: 59
8. Bowmer TN, Tonelli AE (1986) J. Polym. Sci., Part B: Polym. Phys. (1986), 24: 1631
9. Drushel HV, Ellerbe JS, Cox RC, Lane LH (1968) Anal. Chem., 40: 370
10. Sargent M, Koenig JL, Maecker NL (1991) Appl. Spectrosc., 45: 1728
11. Olive GH, Olive S (1979) In: Cantow HJ (ed) Advances in Polymer Science 32. Springer-Verlag, Berlin, p.123
12. Krigbaum WR, Tokita N (1960) J. Polym. Sci., 43: 467
13. Bohn CR, Schaefgen JR, Statton WO (1961) J. Polym. Sci., 55: 531
14. Stuart HA (1952) Die Physik der Hochpolymeren, Vol. 1. Springer-Verlag, Berlin
15. Colthup NB, Daly LH, Wiberley SE (1990) Introduction to Infared and Raman Spectroscopy, 3rd ed. Academic Press, New York
16. Dong L, Hill DJT, O'Donnell, JH (1993) J. Polym. Sci., Part A: Polym. Chem., 31: 2951
17. Dong L, Hill DJT, Whittaker, AK, Ghiggino KP (1994) Macromolecules, 27: 5912