Poly(acrylonitrile-co-methyl acrylate) Copolymers: Correlation Between Copolymer Composition, Morphology and Positron Annihilation Lifetime Parameters

E. Zengeni, P. C. Hartmann, R. D. Sanderson, P. E. Mallon

Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

ABSTRACT: A series of poly(acrylonitrile-co-methyl acrylate) copolymers of differing copolymer compositions are synthesized through free radical emulsion copolymerisation of methyl acrylate (MA) and acrylonitrile (AN) and by variation of the monomer feed ratios. The copolymers are characterized by NMR, SEC, WAXD, DMA, and positron annihilation lifetime spectroscopy. Results show that, there is a linear decrease in the glass transition temperature (T_g) of the copolymers and the MA content. There is also a progressive decrease in the crystallinity of the copolymers with increasing MA content. Positron results show a sigmoidal variation in the ortho positronium lifetime with an increasing MA content. The low MA content, semi-crystalline copolymers show a positive deviation from the linear additive relationship between the o-Ps lifetime and MA content, whereas the higher MA content amorphous copolymers show a negative deviation from the linear additive behavior. The o-PS intensity shows a linear behavior with MA content with a slight deviation from the additive linear behavior for the very high-content MA copolymer. These variations in the measured positron lifetime parameters are interpreted in terms of the copolymer morphology. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1060–1066, 2011

Key words: polyacrylonitrile-co-methyl acrylate copolymers; positron parameters related to glass transition temperature; copolymer composition; structural properties

INTRODUCTION

Polyacrylonitrile (PAN) exhibits remarkable properties such as low-permeability to gases, resistance to most chemicals, and ability to orient. However, it has little applications as homopolymer, because of poor processability that results from a high-melting point and a high-melt viscosity.[1] Copolymerisation has become one of the widely used methods to improve the melt processability of PAN without significantly compromising its desirable properties.[1] During copolymerisation a noncrystallisable comonomer is randomly inserted along the PAN chains so that it alters the close chain packing and the long crystallisable acrylonitrile sequences resulting in improved chain mobility and reduced crystallite size. These acrylonitrile based copolymers have found applications as fiber precursors (e.g. acrylonitrile-methyl acrylate copolymers),[1–4] and packing material (e.g. styrene-acrylonitrile, acrylonitrile-methyl-acrylate copolymers).[1] Copolymerisation gives materials with properties (e.g. crystallinity, molecular relaxation) that are different from those of homopolymers of the monomers used in the copolymerisation.

Many physical properties of polymers have been related to their free volume properties; hence efforts have been made to evaluate and quantify these free volume properties in polymers.[5–9] Positron annihilation lifetime spectroscopy (PALS) has become one of the commonly used techniques in the free volume studies of polymers, because of its high-sensitivity to subnanometer holes.[5,10–15] The size of the free volume hole can be estimated from the o-Ps lifetime using a simple relationship, whereas the o-Ps intensity can be related to the free volume concentration. When positronium is formed, it occupies the free volume holes that have less electron density. The positron eventually annihilates with an electron form the surrounding materials in a process known as "pick-off" annihilation. The o-Ps lifetime is the time the positronium exists in the free volume hole before it picks up an electron and annihilates. This lifetime is directly correlated to the size of the free volume hole. While PALS provides unique information on the polymer free volume, it is not an information rich technique. There is, therefore, a need to correlate PALS parameters to other polymer

TABLE I
Monomers Feed Composition, Acrylonitrile Molar Ratio in the Feed (f_{AN}) and Copolymer's Acrylonitrile Molar Ratio (F_{AN}), Number Average Molecular Mass (Mn), Polydispersity Index (PDI), and T_g of Copolymers of Different Copolymer Composition

Sample	Feed acrylonitrile (mol)	Composition methyl acrylate (mol)	f_{AN}	F_{AN}[a]	Mn $\times 10^5$ (g/mol)	PDI[b]	$T_g{}^c$(°C)
A100	0.16	0.00	1.00	1.00	–	–	104
A90	0.16	0.01	0.90	0.85	–	–	94
A80	0.13	0.03	0.80	0.77	–	–	88
A70	0.11	0.05	0.70	0.68	–	–	83
A60	0.09	0.06	0.60	0.58	3.29	5.84	75
A50	0.08	0.08	0.50	0.46	–	–	63
A40	0.06	0.10	0.40	0.36	3.82	2.76	54
A30	0.04	0.11	0.30	0.28	4.00	2.55	42
A20	0.03	0.13	0.20	0.16	3.80	3.59	35
A10	0.02	0.15	0.10	0.08	3.20	2.67	23.3
A00	0.00	0.16	0.00	0.00	–	–	12.5

[a] Determined using NMR.
[b] PDI = M_w/M_n.
[c] Temperature corresponding to the maximum tan (δ).

properties such as crystallinity and chain mobility, to get a better understanding of the microstuctural properties of the polymer. PALS has been used extensively in miscibility studies of polymer blends[14,16–20] but fewer reports have been made on systematic copolymers.[21–24] Reports on positron parameters in copolymers[22,24] focused mainly on weakly polar polymers emphasizing the effect of polarity on positron parameters (o-Ps lifetime and o-Ps intensity). It was concluded from this work[22,23] that polarity affects o-Ps lifetime through quenching and o-Ps intensity through inhibition. These effects can lead to misleading free volume parameters. These effects were, however, not observed in strong polar polymers like PMMA.[25–27] In this study poly(acrylonitrile-co-methyl acrylate) of various comonomer compositions were synthesized, and their positron parameters were studied and correlated to molecular structure, crystallinity, and chain mobility in terms of T_g. The o-Ps quenching and inhibition effects were considered to have an insignificant effect on the positron parameters in this study because scavengers have influence within a limited concentration.[21,28] Previous reports[17,18,26,29] on positron parameters focused mainly on commercial polymers, but here a systematic copolymer series was synthesized and characterized in conjunction with the positron parameters.

EXPERIMENTAL

Materials

Acrylonitrile (AN) and methyl acrylate (MA) monomers were supplied by Merck both with 99.5% purity. These monomers were passed through an alumina column to remove the inhibitor before use.

Sodium dodecyl sulfate (SDS) was supplied by Aldrich and was used without any purification. Potassium persulfate (KPS) was obtained from Aldrich and was used as received.

Preparation of copolymers

Copolymers of composition varying from 90% AN : 10% MA to 10% AN : 90% MA (mol:mol ratio) were prepared according to the procedure outlined below.

Water (150 mL) was dispersed in a three-neck flask and the two monomers were added into the flask in quantities shown in Table I according to the targeted copolymer composition, (e.g. for sample A90 the target was a copolymer containing 90% AN and 10% MA). SDS (0.76g; 2.6×10^{-3} mols) was added before the mixture was stirred for 30 min under nitrogen. The temperature was then raised to 70°C and after equilibration, 10 mL (3.7×10^{-4} mol) of KPS was added to initiate the reaction. The reaction was run for 2 h at 70°C. The resultant copolymer was precipitated in methanol, and then washed with ethanol and water. Finally, the copolymer was dried under vacuum at 60°C to constant weight.

For all the copolymers the SDS, water, and KPS were kept constant at amounts mentioned in procedure above and the monomer compositions were varied as shown in Table I.

CHARACTERIZATION

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR)

The copolymer compositions were determined using ^{1}H-NMR. The NMR spectra were obtained using a

Varian VXR-Unity 400 MHz instrument. The copolymers were dissolved in deuterated dimethyl sulfoxide (DMSO-d6) and the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as a reference.

The copolymer compositions were calculated as outlined below:

m = AN content in the copolymer

n = MA content in the copolymer

x = the integral, because of the methyl proton from the MA monomer only
y = the integral, because of the methylene protons from both monomers.

Using the peaks indicated in Figure 1

$$n = \frac{x}{3} \qquad (1)$$

$$m = \frac{y}{2} - \frac{x}{3} \qquad (2)$$

Equation 1 gives the amount of MA in the copolymer and eq. (2) gives the amount of AN in the copolymer.

Ratio of MA content in the copolymer $= \frac{n}{n+m}$ and ratio of AN content $= 1 - \frac{n}{n+m}$.

Size exclusion chromatography (SEC)

SEC measurements of copolymers with 60–100% MA content were done on a SEC instrument comprising a Waters 717 plus autosampler, Waters 600E system controller, and Water 610 fluid unit. A Waters 410 differential refractometer was used for detection. Two PLgel 5 μm Mixed-C columns and a PLgel 5 μm guard column were used. The sample volume injected into the column was 100 μL, whereas the oven temperature was kept at 30°C. THF (HPLC grade, BHT stabilized), containing 0.1 M lithium chloride (LiCl) was used as an eluent at a flow rate of 1 mL/min. Calibrations were done using narrow polystyrene standards with a molecular range of 800 to 2×10^6 g/mol and the SEC data is reported as polystyrene equivalents.

The SEC measurements of the copolymer with more than 40% MA content were done using a Waters 150C ALC/GPC chromatograph and a GRAM column. Copolymer weighing 0.02 g was dissolved in N-methyl-2-pyrrolidinone (NMP) and 0.1 M LiCl. A temperature of 70°C and a flow rate of 1mL/min were used.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis, to determine storage modulus (G'), loss modulus (G''), and damping factor ($\text{Tan}(\delta)$) of the copolymer films, was carried out using an MCR 501Anton Paar Rheometer in oscillatory mode, from 180 to 45°C, at a heating rate of -4°C/min, using a 25 mm diameter plate-plate geometry. All tests were done under 0.1% deformation and 10 N normal force at a frequency of 1 Hz. The samples were molded into disk shaped films by compression at 150°C. The thickness of all samples was in the range 0.8–1.0 mm.

Positron annihilation lifetime (PAL) measurements

All positron lifetime measurements were performed at room temperature using conventional fast-fast coincidence system with 250 ps time resolution determined using a ^{60}Co. A 20-μCi ^{22}Na positron source sealed in 6 μm aluminum foil was sandwiched between two circular sample disks of 15 mm diameter and a thickness of at least 1 mm. This sample-source sandwich was placed between two detectors of the spectrometer to acquire the lifetime spectrum. Each spectrum contained approximately a million counts accumulated over 1–1.5 h. All spectra were analyzed into three lifetime components with the help of PATFIT program taking into account the correction for possible annihilation in the positron source.[30] The o-Ps lifetime results were used to obtain the mean free volume hole radius using the empirical equation:[12,31]

$$\tau_3^{-1} = 2\left[1 - RR_0^{-1} + (2\pi)^{-1}\sin\left(\frac{2\pi R}{R_0}\right)\right](ns^{-1}) \qquad (3)$$

where $R_0 = R + \Delta R$, where $\Delta R = 1.66$Å is the thickness of the homogeneous electron layer in which the positron annihilates, τ_3(ns) is the o-Ps lifetime and R (Å) is the hole radius.

Assuming that the probability of o-Ps formation is proportional to the low-electron density regions, the o-Ps intensity (I_3) can be related to the number of free volume holes in the matrix and the fractional free volume can be determined by using equation:

$$f_v = C \times I_3 \times V_f \qquad (4)$$

where C is a constant that can be determined from independent experiment and $V_f = \frac{4}{3}\pi R^3$.

However without using the constant C, relative fractional free volume can be calculated.

$$F_{vR} = V_f \times I_3 \qquad (5)$$

The use of positron parameters in relation to free volume parameters has been reported to be justified

only if there are no other chemical processes that come into play to inhibit the formation of the o-Ps.[12,23,32] This is because of the fact that, if o-Ps inhibition or quenching, these processes affect the o-Ps intensity.
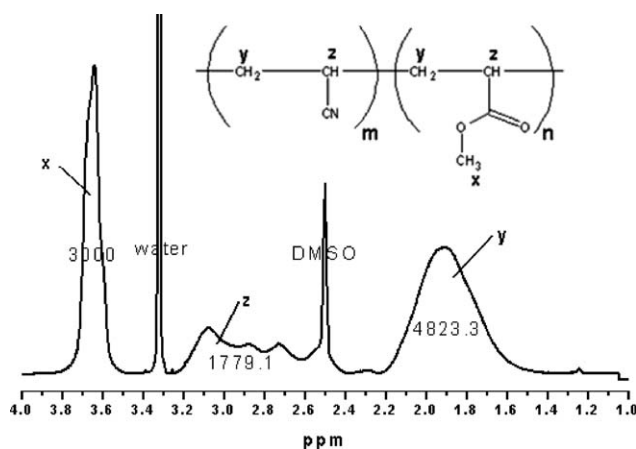
RESULTS AND DISCUSSION

^{1}H-NMR results were used to calculate the copolymer composition over the entire composition range used. Figure 1 shows the ^{1}H-NMR of 60%AN : 40%MA copolymer (mol:mol).
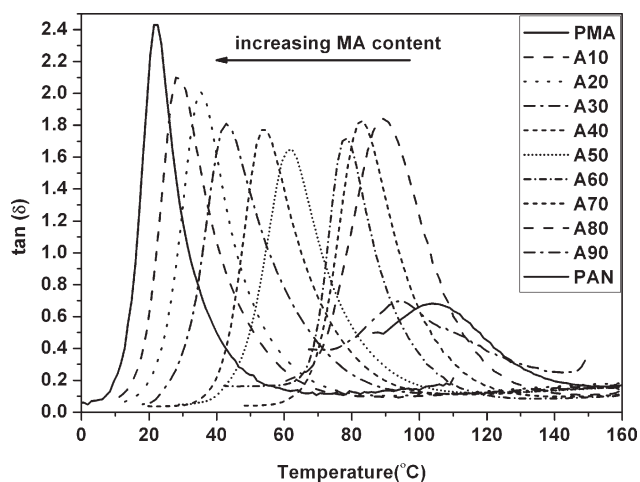
The peak in the region 3.6–3.8 ppm is because of the resonance of the protons of the methoxy group of MA units only, whereas the protons of the methylene units from both comonomer units gave the broad peak at 1.6–2.2 ppm. The protons of the methine units of both comonomers gave a peak in the region 2.6–3.2 ppm. The single peak at 3.3 ppm is because of traces of water in DMSO-d$_6$. The methoxy peak and the methylene peaks were used to calculate the copolymer compositions of the copolymers according to eqs. (1) and (2). The copolymer composition results are shown in Table I.

Table I shows that the number average molar mass of the copolymers were high in the range of 3.2×10^5–4.0×10^5 g/mol typical of emulsion polymerization reactions. The high AN content copolymers were not soluble in THF, hence their molar masses were difficult to obtain via SEC. Their Mn values are omitted except for copolymer with 60% AN whose Mn was obtained with help from another laboratory using NMP as a mobile phase in the analysis.

The T_g of the copolymers was taken from the temperature corresponding to the maximum of the tan (δ) curves determined from DMA. These curves are shown in Figure 2. The onset of T_g and the T_g values of the copolymers decreases linearly with increasing
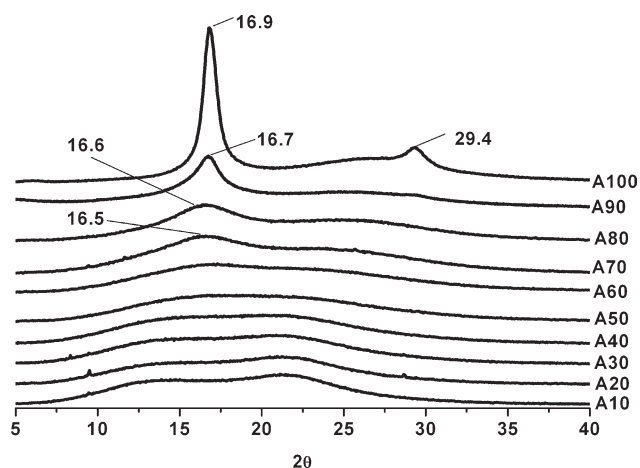
Figure 2 DMA tan (δ) curves of the poly(acrylonitrile-co-methyl acrylate) copolymers.

comonomer (MA) content as shown in Table I. The MA is randomly inserted along the AN chain thus enhancing the molecular motions of the chains. The AN chains are stiff, because of the intermolecular dipole-dipole interactions between CN groups of monomer units in the helical conformations of the chains.[33,34] The main chains of PAN are tightly packed so that the intermolecular spaces in the amorphous regions are reduced and the triple bond of the cyano group restricts free rotation leading to molecular stiffness hence a high T_g for PAN. The introduction of the bulky methoxy pendant group in the AN results in disruption of the AN chain causing an improvement in the chain mobility and hence the observed reduction in the T_g of the copolymer.

The crystallinity of the copolymers was also found to decrease with increasing MA content as would have been expected.[35,36] Figure 3 shows the WAXD of the copolymers. The homopolymers PAN shows

Figure 1 ^{1}H-NMR spectra of poly(acrylonitrile-co-methyl acrylate) containing 40% MA (Solvent: DMSO$_{-d6}$).

Figure 3 WAXD results of poly(acrylonitrile-co-methyl acrylate) copolymer of different compositions.

two crystalline peaks at $2\theta = 17°$ and $2\theta = 29°$ as was reported elsewhere.[33,35,37] The crystallinity of the PAN has been attributed to parallel alignment of molecular rods, which results from the irregular helical conformation of PAN macromolecular chains through intermolecular dipole-dipole interactions between nitrile groups.[33,34] Upon incorporation of MA, these two crystalline peaks decrease in intensity and became broader until they are completely diffuse. The MA causes changes in the crystalline lattice if a critical amount is reached through interruption of the long range AN sequence as it gets randomly inserted along the AN chain and because of the imperfections at crystalline boundaries produced by the bulkier comonomer. As the MA content increases, the average length of uninterrupted AN sequence decreases and so does the crystallinity of the copolymer. The insertion of the random MA units essentially decreases the longest crystallizable AN sequences.

Figure 4(a) is a 3D plot relating o-Ps lifetime (τ_3), T_g and MA content, whereas Figure 4(b) shows a correlation between the MA content and o-Ps lifetime. The PAL spectra were recorded for PAN and PMA homopolymers and copolymers of different comonomer compositions at 25°C. The spectra could only be resolved into three components for all samples not four components as reported for other crystalline polymers.[5,38]

It was found that upon addition of MA the T_g of the copolymers decrease, whereas the o-Ps lifetime increase. Although the o-Ps lifetime values of the copolymers fall between those of the homopolymers, deviation from the linear additive vaules (solid line) is observed. The general increase in the o-Ps lifetime followed a sigmoidal curve with increasing MA content as shown by the dotted graph in Figure 4(b) These fitted lines (the solid and the dotted) are included in this Figure solely as a guide, to clarify the relation between the parameters being studied as well as the deviation of the actual values from the expected theoretical additive value.

Below 50% MA content, there was a positive deviation from linearity with increasing MA content, whereas above 50% MA a negative deviation was observed with increasing MA content. The o-Ps lifetime shows a sharp increase with increasing MA content from 0 to 30% MA. This is because of the enhanced mobility of molecular chains in the amorphous regions and the disruption of the crystalline structure of the long range AN chain. The PAN homopolymers chains are known to be closely packed because of the polarity of cyano group and the incorporation of MA disrupts this close packing causing an increase in the hole size.[34,35] The crystalline phases in the crystalline copolymers contain only AN units. This process effectively "phase segre-
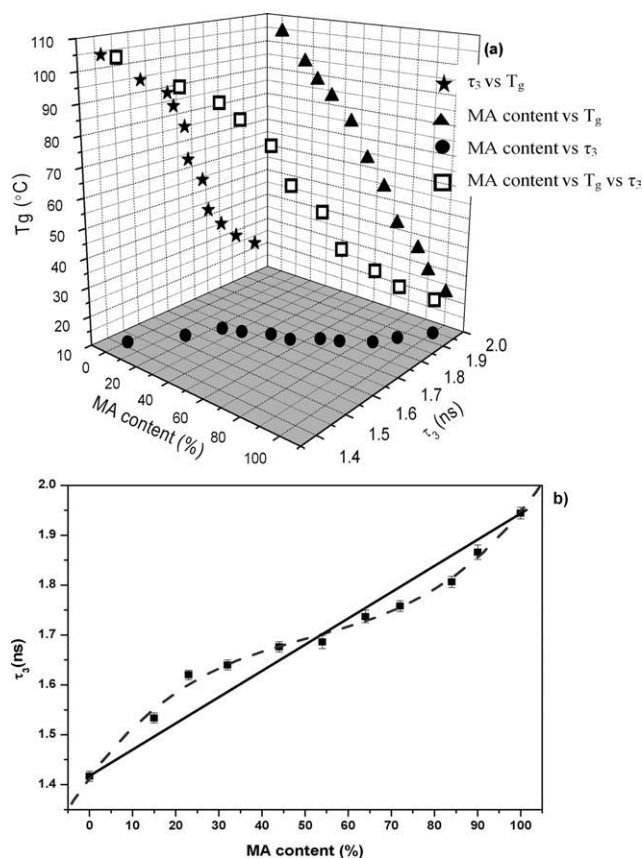
Figure 4 (a) The effect of MA content on T_g and o-Ps lifetime, (b) relationship between MA content and o-Ps lifetime of the different poly(acrylonitrile-co-methyl acrylate) copolymers. (Lines included as a guide only).

gates" the AN rich segments in the crystalline area from those with higher MA content that are predominantly in the amorphous region. The amorphous phase contains more MA relative to the crystalline phases and relatively more MA than would be expected from the additive copolymer composition. As the o-Ps predominantly annihilate in the amorphous phase, this leads to an apparently "higher" o-Ps lifetime than would be expected from the copolymer composition and the observed "positive deviation". The larger volume pendant group of the methoxy group of the MA unit is capable of increasing the free volume hole size.[22]

Between a 40 and 60% MA content, the increment gradient in lifetime is reduced so that an inflection from positive to negative deviation from linear additive behavior is observed in this region. The onset of the inflection in the τ_3 (o-Ps lifetime)–MA content curve corresponds to the point where the disappearance of crystallinity peaks is observed in the WAXD spectra of the copolymers. However some crystallinity still remains. In this region, the incorporation of MA has a larger effect on the free volume hole number (I_3) rather than the hole size as clearly seen in Figure 5. This could be a result of the larger volume
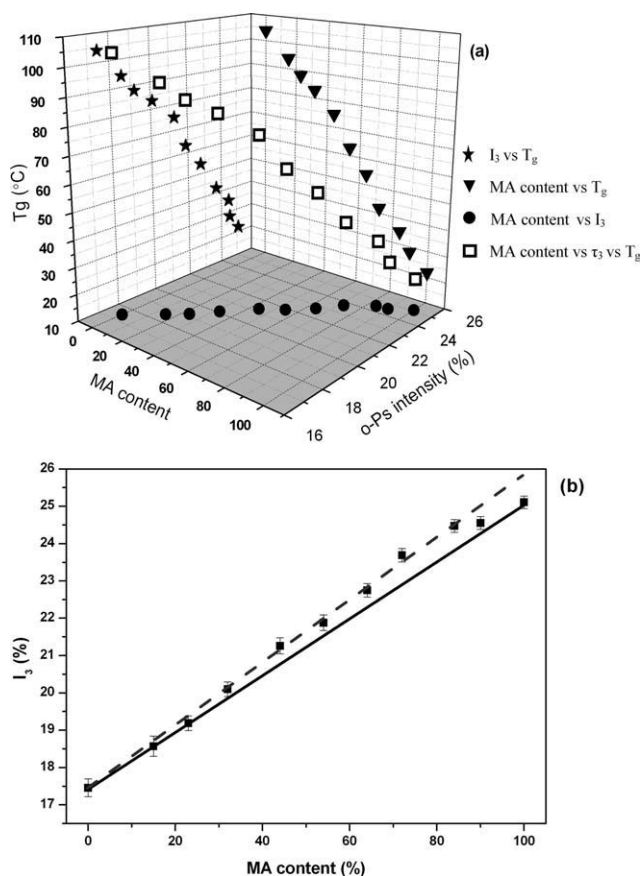
Figure 5 (a) The effect of MA content on T_g and o-Ps intensity, (b) relationship between MA content and o-Ps lifetime for poly(acrylonitrile-co-methyl acrylate) copolymers. (Lines included as a guide only).

methoxy group, which is incorporated randomly along the AN chain causing an increase in the hole number rather than hole size, because of the steric hindrance effects.

From 70 to 100% MA a negative deviation of the o-Ps lifetime (τ_3) from linearity was observed. These copolymers are essentially amorphous with little to no crystallinity present. Similar negative deviation from the additive behavior have been reported in polymer blends has been attributed to miscibility of these blends,[39] because of the changes in molecular packing interactions[9] and favorable segmental conformations.[7] The negative deviation observed here could result from the intermolecular interactions from the methoxy groups and cyano groups in chains that cause enhanced molecular packing, hence a decreased free volume hole size compared with that expected. There is, however, a continuing increase in o-Ps lifetime with increasing MA content. This is as a result of the increased steric hindrances and repulsions with increasing number of methoxy groups having a more significant effect on the hole size.

The o-Ps intensity shows a more positive linear dependence on the MA content and T_g as shown in Fig-

ures 5(a,b) until 80% MA, from where it starts to show a slight deviation from linearity (the dotted line). However, this linear relationship deviates from the theoretical additive linearity (the solid line). (The equations of both lines were calculated using Origin 7.5 program ($R^2 = 0.997$) and are included only as a guide).

Most of the copolymers studied here are glassy, that is, the experiments were done below their T_g except for the copolymer with 90% MA copolymer and the PMA homopolymer. We would expect the changes in chemical composition, which enhance chain mobility to have the same effect as that reported for temperature variations below T_g.[6] An increase in temperature in the regions of restricted mobility ($T < T_g$) results in an increase in free volume hole number rather than an increasing free volume hole radius. In this copolymer system, the addition of the MA monomer caused an increase in the hole number (I_3) in the 40–60% MA content region where the lifetime (τ_3) remained almost constant. Above 80% MA the PAL measurements were conducted above the T_g of the copolymers. As reported earlier,[6] increased temperature above T_g results in an increase in the hole size rather than hole number. In this case, a similar argument could be made for the deviation from linearity in o-Ps intensity at higher MA content and an increase in o-Ps lifetime, although the effects of the increasing MA content should also be taken into account.

Equation 5 was used to calculate the relative fractional free volume in the different copolymers and the results were plotted against T_g as shown in Figure 6. The fractional free volume also follows a sigmoidal curve with decreasing T_g as shown in
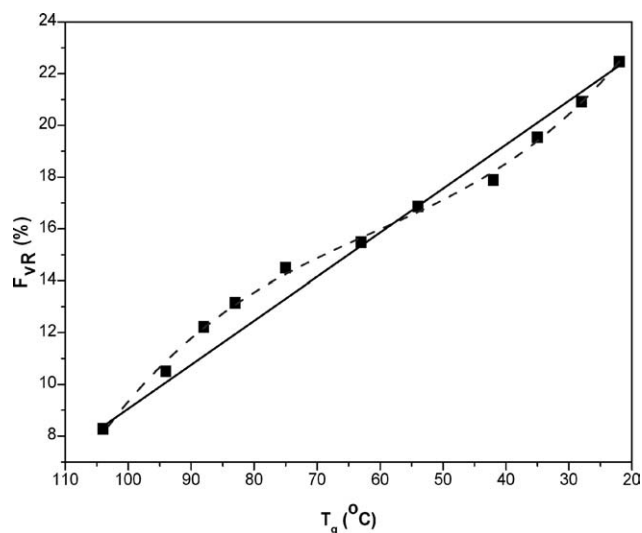
Figure 6 Variation of relative fractional free volume [determined from eq. (5)] for poly(acrylonitrile-co-methyl acrylate) as a function of increasing MA content and T_g. (Lines included as a guide only).

Figure 5. Below 50% MA content the fractional free volume shows a slight positive deviation from linearity, whereas above 50% MA a negative deviation from linearity was observed. The fractional free volume follows this sigmoidal variation as a result of the variation in the o-Ps lifetime.

CONCLUSION

The free volume properties, the crystallinity and the T_g of poly(acrylonitrile-co-methyl acrylate) copolymers are dependent on the copolymer composition. Copolymers containing more than 60% AN had a crystalline reflection peak in WAXD, whereas those with less than 60% did not exhibit any crystalline peak thus showing a total disruption of crystallinity in copolymers with high MA content. The T_g decreased linearly with increasing MA content, because of the enhancement of chain mobility. The o-Ps lifetime followed a sigmoidal increase with increasing MA content. There is a positive deviation at low MA contents and a negative deviation at higher MA content. The inflection point corresponds to the disappearance of the crystalline peak. This means that the positive deviation is observed in the semi-crystalline copolymers (effectively because of the higher apparent MA content in the amorphous phase). The negative deviation resulted from intermolecular interactions, but these interactions decreased with increasing MA content so that an overall increase in o-Ps lifetime was observed. This deviation of o-Ps lifetime with regards MA content is despite the linear relationship between the MA content and T_g. There is, however, a linear dependence between o-Ps intensity and MA content and T_g up to copolymers with T_g below the measurement temperature. The increases in o-Ps (related to the free volume hole size), o-Ps intensity (related to free volume hole number), and the fractional free volume are a result of improved chain mobility and reduced packing brought about by disruptions in the AN sequence upon MA incorporation.

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