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A thermally-stimulated-current study of ethylene-methyl-methacrylate copolymers

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Two ethylene-methyl methacrylate (EMMA) copolymers were studied by infrared (i.r.) spectroscopy, Differential Scanning Calorimetry (DSC) and Thermally Stimulated Currents (TSCs). The critical temperature, T_c, relaxation time, τ_c (measured in seconds), and Degree of Disorder (DOD) of the polymers were also measured by Relaxation Map Analysis (RMA). The i.r. and DSC results showed that these two copolymers are random copolymers with a melting point, T_m, at 82.6 °C for a sample containing 18 wt % methyl methacrylate (EMMA18), and at 53.0 °C for a sample having a MMA content of 38 wt % (EMMA38). From TSC spectra analysis, EMMA18 showed a glass-transition point, T_g, at -41.0 °C, whereas EMMA38 had a T_g at -36.0 °C together with a γ-relaxation at -120 °C. Both samples have their space charges in the range 5–30 °C. The RMA showed that EMMA18 has $T_c = -5.74$ °C, $\log \tau_c = -2.90$ (τ in seconds) and DOD = 54.65. EMMA38, however, has $T_c = -15.71$ °C, $\log \tau_c = -1.59$ and DOD = 48.69. The absence of γ-relaxation in EMMA18 was explained by evidence that it has a higher DOD. While the low mechanical properties of EMMA38 were mainly attributed to the contribution from the short chain segments, demonstrated by its low T_c.

1. Introduction

Owing to its stability to light and heat, Polyethylene (PE) has been used to prevent steel from corrosion by coating it onto the surface of iron and steel. However, the lower polarizability of the main chain reduces the adhesion strength between the polymer and the steel surface. The adhesion strength can be increased in two ways. One is by grafting a polar group such as maleic anhydride, acrylic acid, onto PE as a side chain. The other way is to copolymerize the polar groups into the PE main chain. The disadvantage of grafting polar groups onto PE is that a high percentage cannot be obtained, normally less than 5 wt % [1]. However, in the case of copolymerization, the comonomer content can be varied as required. An EMMA copolymer, owing to its stability at high temperature, has been used either as its proto-type, or co-extruded or blended with other polymers. In either case, mechanical properties are governed by the crystallinity and the molecular weight of the copolymers [2]. It is also generally accepted that the comonomer content not only affects the crystallinity (the melting point), but also affects the glass-transition point. In this way the mechanical properties have been shown to have some relationship to the glass transition; therefore the glass-transition behaviour was examined by choosing different methyl methacrylate (MMA) contents for EMMA copolymers to test their effect on the physical properties of the copolymers.

Thermally stimulated currents or thermally stimulated depolarization currents (TSCs or TSDCs) have been adopted as tools for probing ionic crystals, using dipole orientation, by Bucci *et al.* [3] in 1964 (they called them ionic thermocurrents). The advantage of this technique is its high sensitivity ($10^{-12} \sim 10^{-13}$ A cm^{-2}) even at low frequencies (10^{-3}–10^{-4} Hz), this leads to enhanced resolution of the different relaxation processes. These techniques have made great progress in several laboratories and they have been applied in the study of many polymers [4], additive effects [5], and polymer blends [6].

Several reports [4, 6] have demonstrated the advantage of thermal windowing (or Relaxation Map Analysis (RMA)): the possession of the programmable nature of the initial global spectra, which allows inspection of specific transitions of interest. Analysis of spectra by thermal windowing has, to date, led to marginal accuracy for the activation energy, E_a, of the relaxation process. Excellent agreement for values of E_a obtained by thermal windowing of TSC spectra and by dielectric and dynamic mechanical measurements has been reported by Sauer *et al.* [7], not only for low-temperature transitions but also for higher temperature transitions such as the glass transition.

In a report by Ibar [8], polymethyl methacrylate (PMMA) has been shown to have two compensation points, one is positive and the other is negative. The two compensation points are also shown in graphs of enthalpy of activation with entropy of activation. By intersecting the two compensation points, the most probable glass-transition point, T_g, can be obtained.

To know if these phenomena also exist in the copolymers of ethylene with methyl methacrylate, EMMA was also examined by the same method using different methyl-methacrylate contents.

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2. Experimental procedure

2.1. Materials

Two EMMA copolymers which are synthesized by a high-pressure-radical process were used as the samples; they were purchased from the Sumitomo Chemical Company. Their physical properties are listed in Table I.

2.2. Infrared spectroscopy

The i.r. spectra were measured with a JASCO i.r. spectrometer A-100 from $650\,\mathrm{cm}^{-1}$ to $4000\,\mathrm{cm}^{-1}$ with thin polymer film 0.050 mm thick.

2.3. Differential scanning calorimetry (DSC)

The melting points of the copolymers were measured using a sample weight of about 14 mg in a Perkin-Elmer DSC-7 at a heating rate of $10\,^{\circ}\mathrm{C\,min}^{-1}$ from 45 to 120 °C with the samples in an aluminium crucible. The melting points were taken as the peaks of the DSC spectra.

2.4. TSC measurement

A TSC/RMA spectrometer, model 41000 (Solomat Instrument, CT) was used for these experiments. This instrument covers the temperature range of -180–400 °C. The samples were pressed into thin films under pressure at about 100 °C, then doped with silver lacquer and shielded by a Faraday cage; they were all evacuated to $\sim 10^{-2}$ Pa prior to the experiment and also were flushed with high purity helium.

2.4.1. Global spectra

In the global spectra test, the samples were polarized by an electric field ($E = 200 \sim 600\,\mathrm{kV\,m}^{-1}$) at the polarization temperature, T_p, for 2 min and then quenched to the freezing temperature with a Newtonian cooling rate (that is, as quickly as possible). After the field was turned off, the sample was short circuited and the depolarization current, due to dipole reorientation, was measured at a heating rate of $7\,^{\circ}\mathrm{C\,min}^{-1}$ until the sample reached its final temperature.

2.4.2. Relaxation map analysis (RMA)

RMA was performed by applying an electric field ($E = 200\,\mathrm{kV\,m}^{-1}$) at T_p for 2 min, then the sample was quenched to $T_p - 5\,^{\circ}\mathrm{C}$ and depolarized for 2 min. After that, the sample was cooled to 40 °C below this polarization–temperature window, and the depolarization spectrum of this narrow distribution of relaxation was then measured at a heating rate of $7\,^{\circ}\mathrm{C\,min}^{-1}$ until a temperature about 30 °C above T_p was reached.

TABLE I Physical properties for samples of EMMA18 and EMMA38

Sample	MMA (wt %)	MI[a] (kg/10 min)	Density ($\mathrm{kg\,m}^{-3}$)	Tensile strength ($\times 10^4\,\mathrm{kg\,m}^{-2}$)
EMMA18	18	0.007	940	90
EMMA38	38	0.050	950	10

[a] Melt index

The analysis of the TSC spectra by Bucci is based on a theory of single Debye relaxation. In his work, if the sample was polarized at a temperature T, the polarization would have a value P_0 after an infinite time; thus the decay of the polarization after removal of the field is given by

$$P(t) = P_0 \exp(-t/\tau(T))$$

the corresponding depolarization current is

$$J(t) = -\,\mathrm{d}P(t)/\mathrm{d}t$$

so that $J(t) = P(t)/\tau(T)$.

If $\tau(T)$ can be expressed by an Arrhenius equation, then

$$\tau(T) = \tau_0 \exp(E_a/kT)$$

where τ_0 is a pre-exponential factor, E_a, an apparent activation energy, and k the Boltzman constant.

When several Arrhenius lines converge into one single point, that point is called a *compensation point*. In general, this is a characteristic property of amorphous polymers or of the amorphous region in semicrystalline polymers. From an Arrhenius plot, the enthalpy of activation and the entropy of activation can be determined. One can define the DOD from the entropy versus enthalpy, ΔS versus ΔH, graph when T_p is varied. Actually the value when $\Delta H = 0$ should be used, but it can be shifted by an arbitrary amount, say 100, to make all the numbers positive. Thus one may calculate the DOD (in $\mathrm{cal\,deg}^{-1}$) from the compensation-point co-ordinates $\log \tau_c$, T_c

$$\mathrm{DOD} = 100 - 2 \times [\ln(T_c \times \tau_c) + 23.76)]$$

This DOD may be used to reflect the degree of compatibility of a blend or between the two phases of a block copolymer [8].

3. Results and discussion

To determine the structure of the copolymers, samples were measured by i.r. spectroscopy, the result is shown in Fig. 1. The peak at $720\,\mathrm{cm}^{-1}$ is known to be responsible for the crystallinity of PE, since in high density PE, (which has long ethylene segments in the main chain) this peak is split into two very sharp peaks, while the ethylene copolymer, where the ethylene segments are interrupted by the comonomer, does not show this phenomenon [9]. As shown in Fig. 1, the peak at $720\,\mathrm{cm}^{-1}$ exhibits no split, indicating that the samples are random copolymers of ethylene and methyl methacrylate.

The melting points of these two copolymers were also measured by DSC at a heating rate of $10\,^{\circ}\mathrm{C\,min}^{-1}$; the results were 53.0 °C for EMMA38 which has a MMA content up to 38 wt %, and 82.6 °C for the sample of EMMA18 which has a MMA content of 18 wt %. It is known that an increase of melt flow ratio (MFR) in the copolymer does not change the crystallinity, the melting point or the density [2];

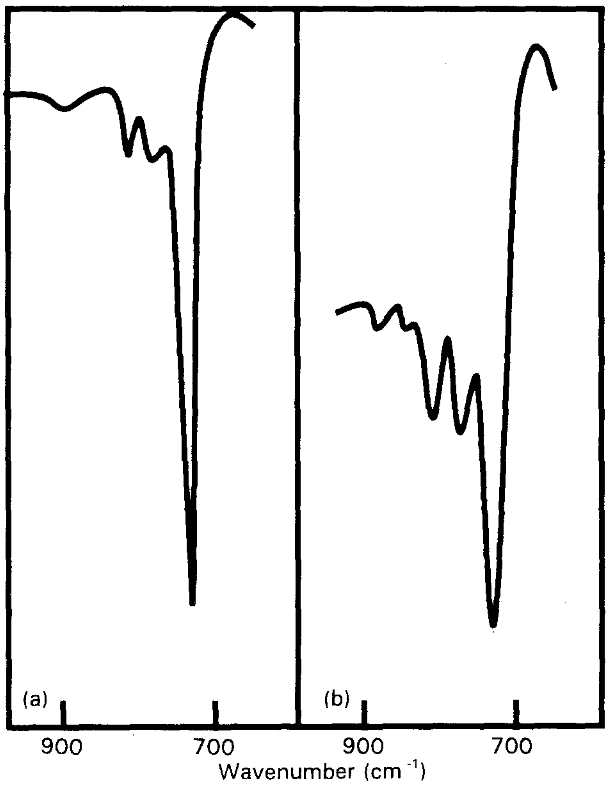

Figure 1 I.r. spectra of: (a) EMMA18, and (b) EMMA38.

so the difference in the melting points may be explained by the different incorporation of MMA into PE chain segments. To know more about the effect of the MMA content on the glass-transition behaviour, the two copolymers were measured by TSCs with RMA.

3.1. TSC global spectra

The TSC global spectra of EMMA18 and EMMA38 were polarized at 35 °C with 200 kV m^{-1} for 2 min and measured from −100 to 50 °C at a heating rate of 7 °C min^{-1}; the results are shown in Fig. 2. From Fig. 2, EMMA18 shows two peaks, one at −41.0 °C and the other at 30.0 °C. While the TSC global spectrum of EMMA38 exhibits a broad small peak at −125–100 °C, two other peaks appear at −41.0 °C and 25.0 °C. However, when the EMMA38 sample was polarized at 0 °C as shown in Fig. 3, the peak at −41.0 °C was shifted to −36.0 °C and the peak at 25.0 °C was shifted to 5.0 °C. The results are summarized in Table II.

It is generally accepted that TSC spectra may arise from dipole reorientation as well as the migration of impurities, and ionic conductors in the polymer (the space charge). One way to differentiate between these mechanisms is to examine the relationship between the peak intensity and the polarization voltage. The results are shown in Fig. 4 for the peaks in the temperature range 0–80 °C. From Fig. 4, the peak intensity shows no linearity with increases of the polarization voltage, indicating that the peaks at higher temperatures for the two EMMA copolymers are due to the space charge. While in Fig. 5, the peak intensities increase linearly with increases in the polarization voltage for peaks appearing at low temperatures. Therefore, the peaks at −41 °C and −36 °C can be attributed to the glass-transition point of EMMA18, and EMMA38, respectively.

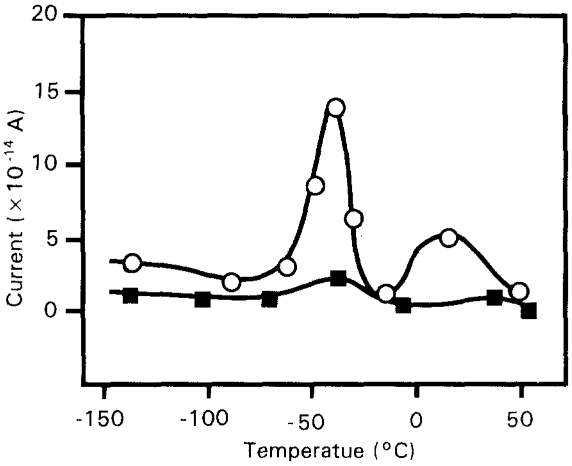

Figure 2 TSC global spectra of: (■) EMMA18 and (○) EMMA38. They were obtained at $T_p = 35$ °C, $t_p = 2$ min and $E_p = 200$ kV m^{-1}.

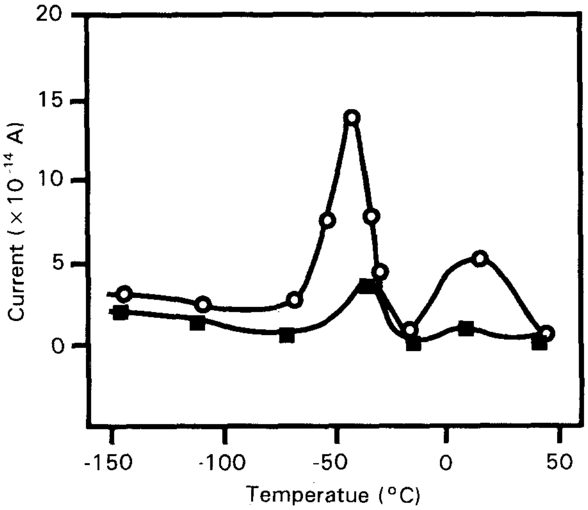

Figure 3 Temperature dependence of the TSC global spectra for EMMA38 obtained at $t_p = 2$ min and $E_p = 200$ kV m^{-1}: (○) $T_p = 35$ °C, and (■) $T_p = 0$ °C.

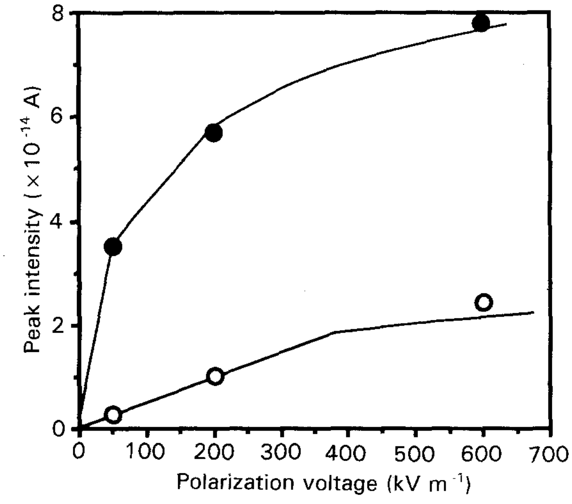

Figure 4 Relationship between peak intensity and polarization voltage for the TSC spectra at 0–80 °C: (●) EMMA38, and (○) EMMA18.

TABLE II Results of TSC global spectra of EMMA18 and EMMA38

Sample	$-125 \sim -100\,^\circ$C	$-100 \sim 0\,^\circ$C	$0 \sim 80\,^\circ$C	T_p(°C)
EMMA18	No peak	− 41.0	30.0	35
EMMA38	Small peak	− 41.0	25.0	35
	Small peak	− 36.0	5.0	0

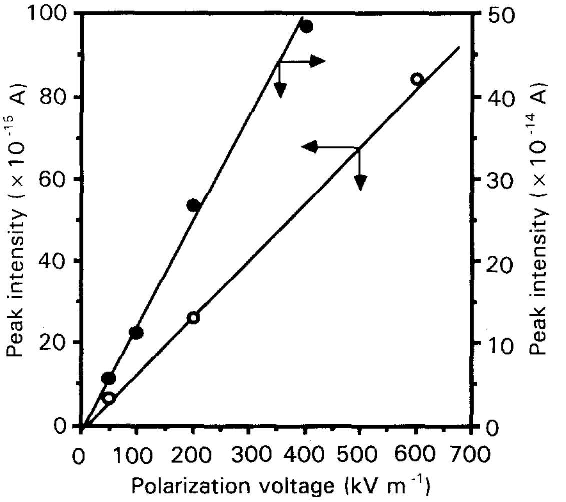

Figure 5 Dependence of peak intensity on the polarization voltage for the TSC spectra obtained at 0 to − 100 °C: (○) EMMA18, and (●) EMMA38.

Generally, the polarization temperature was chosen at a point above the main transition one wished to observe. Under this temperature equilibrium will occur between the fast and slow dipoles; therefore, the peak temperature may be changed according to the polarization temperature [10]. As observed in the EMMA38 sample when polarized at 35 °C, the peak at 25.0 °C is very high and broad; nevertheless, lowering T_p to 0 °C, the peak becomes sharp and shifts to 5.0 °C. Another explanation for the broad peak at 25.0 °C for EMMA38 may be that the polarization temperature is very close to the melting point (53.0 °C); therefore, when heated to close to this temperature, where the space charge has more free volume to move, the complex neutralization of the space charge merged into a broad peak. Because of its high melting point (up to 82.6 °C), EMMA18 did not show this phenomenon.

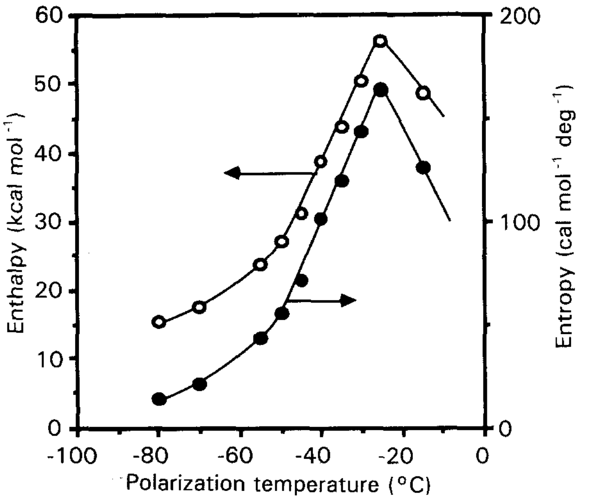

Figure 6 Compensation search for the RMA of EMMA18. The single lines correspond to various polarization temperatures T_p from −80 to −15 °C: (○) enthalpy, and (●) entropy.

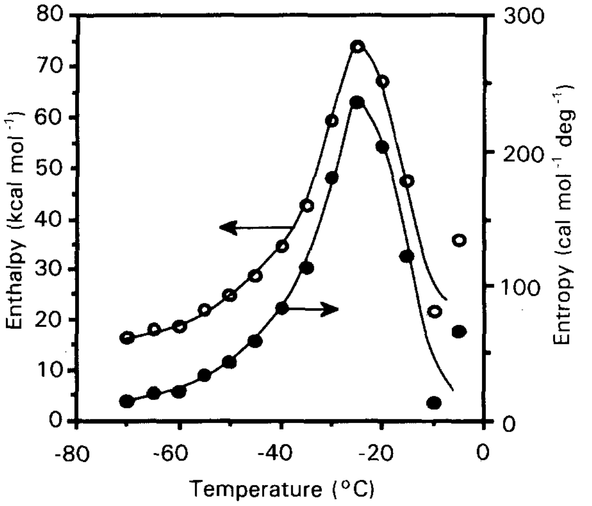

Figure 7 Compensation search for RMA of EMMA38. The single lines correspond to various polarization temperature T_p from −70 to −5 °C: (○) enthalpy, and (●) entropy.

It is also noted that copolymers with high MMA content show higher peak intensities than copolymers of low MMA content; this is reasonable because polar MMA units are easily polarized. However, as mentioned by Ronarch in a study of high density PE and ethylene–propylene rubber (with 45% ethylene), a γ-relaxation due to the local motion in PE was found at a broad peak centred at −123 °C [4]. The peak around −120 °C for the EMMA38 sample should be attributed to the same mechanism. Nevertheless, samples of EMMA18, which has high ethylene content (up to 82 wt %), do not show this peak. One explanation for this is that MMA segments have been more randomly distributed in the ethylene segments for the EMMA18 sample. This will be discussed in more detail in the next section.

In the previous discussion, we have shown that the difference between the melting points is 20 °C, while the difference is only 5 °C for the glass-transition point. It is also observed that EMMA18 samples which have lower MMA content, do not show local motion in PE segments. To know more about the comonomer distribution in the main chain, samples were also analysed by RMA for the peaks at α-transitions.

3.2. Relaxation map analysis

RMA for the EMMA18 and EMMA38 samples are shown in Figs 6 and 7, respectively. From Fig. 6, the activation energy E_a and log τ for EMMA18 are calculated to be 0.5–2.5 eV and −15 to −50 (s), respectively. While from Fig. 7, for the EMMA38 sample

$E_a = 0.5$–3.2 eV and $\log \tau = -15$ to -65. These results show that they are all coming from the same molecular relaxations and the relaxation times do not fit the expected Debye relaxation time are said to be owing to the cooperative effect [11]. When the Arrhenius lines converge to one point that point is called the compensation point. The compensation points for these two copolymers are listed in Table III.

In some way, the assumption of a compensation law in polymers is based on the possibility of a process where chain segments of increasing length contribute at increasing temperatures until a maximum size is reached at the compensation temperature [12]. By comparing the results shown in Table III, T_c for the EMMA38 sample is lower than that for EMMA18; that is, the critical segment length for EMMA38 is shorter than for EMMA18. While EMMA18 having a much lower relaxation time than EMMA38 may be attributed to the more cooperative effect of the polar MMA segments.

It has been pointed out that a same molecular origin can be considered as responsible for mechanical and dielectric relaxations in accordance with the compensation-law analysis [11]. The short chain segments for EMMA38 may be responsible for its low mechanical properties, shown in Table I.

From Table III, EMMA18 (which has lower MMA segments) possesses a higher DOD (54.65) than that for EMMA38 (48.69). As discussed in the analysis of global spectra, EMMA18 which has an MMA content of 18 wt % does not show local motion in PE segments, while EMMA38 which has a MMA content up to 38 wt % does show this phenomenon. This is best explained by the evidence that EMMA18 has a higher DOD than EMMA38. That is, the MMA segments are randomly distributed in PE segments for the EMMA18 sample.

3.3. Eyring transformation and thermokinetic functions

The Arrhenius lines obtained from RMA can be analysed further using an Eyring transformation to yield thermokinetic functions such as the entropy, ΔS, enthalpy, ΔH, and the Gibbs free energy, ΔG, of activation. In this analysis, $\log \tau$ is replaced by $\ln \tau + \ln(k/h) + \ln T$ and plotted against $1/T$: ΔH is proportional to the gradient. The entropy, ΔS, is proportional to the intercept. The Gibbs free energy, ΔG, is calculated from $\Delta G = \Delta H - T_p \, \Delta S$, where T_p is the polarization temperature. From the results plotted in Figs 8 and 9 for EMMA18 and EMMA38, respectively, as T_p increases both ΔS and ΔH (for EMMA18 and EMMA38) increase to a maximum at $T_p = -25\,°C$ and then they decrease. The maxima reveal information about the amorphous state around the glass-transition temperature of a specific polymer.

TABLE III Compensation results for the EMMA18 and EMMA38 samples.

Sample	T_c (°C)	τ_c log(sec)	DOD (cal °C^{-1})
EMMA18	− 5.74	− 2.90	54.65
EMMA38	− 15.71	− 1.59	48.69

The entropy versus enthalpy graphs in Figs 10 and 11 (which are cross plots of Figs 8 and 9) are another way of describing the compensation phenomena.

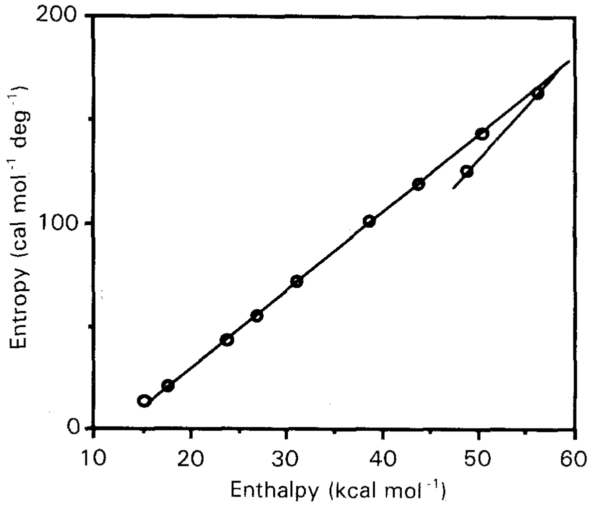

Figure 8 Dependence of enthalpy and entropy on the polarization temperature from −80 to −15 °C for EMMA18.

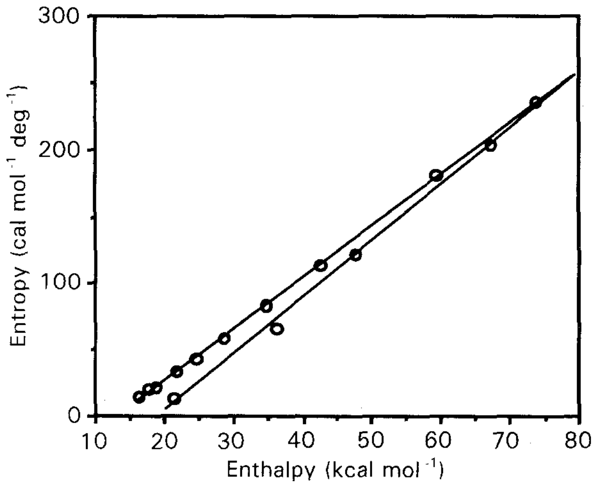

Figure 9 Dependence of enthalpy and entropy on the polarization temperature from −70 to −5 °C for EMMA38.

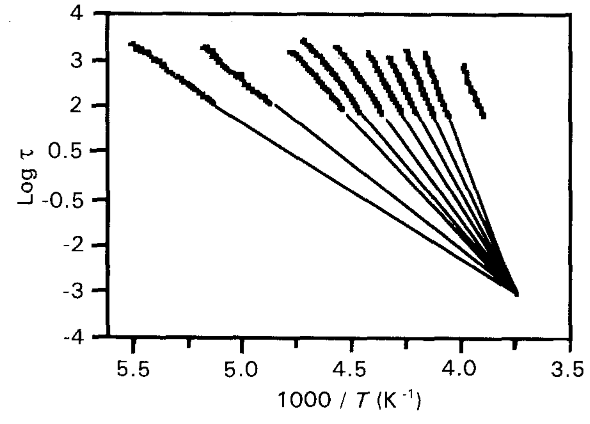

Figure 10 A graph of enthalpy against entropy for EMMA18. The single points correspond to various polarization temperatures, T_p, from −80 to − 15 °C. T_c = − 5.74, $\log \tau_c$ = − 2.9, DOD = 54.65.

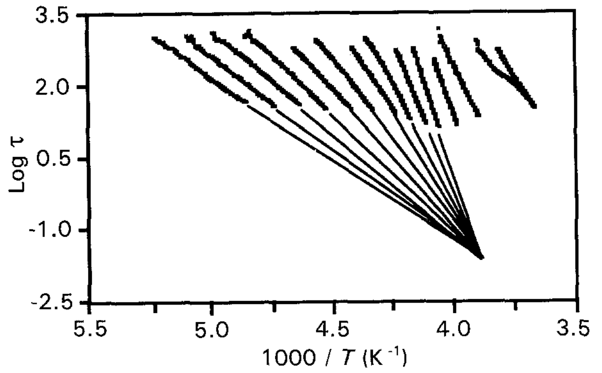

Figure 11 A graph of enthalpy against entropy for EMMA38. The single points correspond to various polarization temperatures, T_p, from −70 to −5 °C. $T_c = -15.71$, log $\tau_c = -1.59$, DOD = 48.69.

TABLE IV Thermokinetic parameters calculated for EMMA18 and EMMA38

Sample	ΔS_g (cal °C mol^{-1})	ΔH_g (kcal mol^{-1})	ΔG_g (kcal mol^{-1})	T_g (°C)
EMMA18	171.6	57.5	16.66	−35.0
EMMA38	261.0	80.0	16.92	−31.3

Figs 10 and 11 show that there are two compensation lines, one with a positive and the other with a negative gradient. The intersect of the positive and the negative lines is the point which describes the behaviour of the glass-transition. Taking the empirical results for many polymers, T_g can be calculated by the following equation.

$$T_g = \frac{(\Delta H_g - a)}{(\Delta S_g + b)}$$

Where $a = 0$ and $b = 70\,\text{cal}\,\text{K}^{-1}\,\text{mol}^{-1}$ [8]. The results calculated for EMMA18 and EMMA38 are listed in Table IV.

It was found that, at the glass-transition point, EMMA38 has much higher enthalpy, entropy and Gibbs free energy of activation than EMMA18 has. It was also noted that the calculated T_g shows some discrepancy with the peak obtained from TSC global spectra; this discrepancy may be explained by the b value not being adequate, or the polarization process being different in the TSC global spectra and RMA spectra.

Nevertheless, both values are comparative and the value obtained by RMA should more precisely reflect the probable glass-transition point.

4. Conclusions

Copolymers of ethylene and methyl methacrylate have been analysed by i.r., DSC and a TSC process together with RMA. The results are summarized as follows.

1. TSC global spectra of EMMA18, which has a MMA content of 18 wt %, had a T_g at −41.0 °C and a space charge at 30.0 °C. However, EMMA38, which has a MMA content of up to 38 wt %, not only had T_g at −36.0 °C and a space charge at 5–30 °C, but also showed local motion in PE at −120 °C.
2. RMA of EMMA18 and EMMA38 showed that EMMA18 has $T_c = -5.74$ °C, log $\tau_c = -2.90$ (sec) and DOD = 54.65, while EMMA38 has $T_c = -15.71$ °C, log $\tau_c = -1.59$ (sec) and DOD = 48.69.
3. The absence of local motion in PE segments for the EMMA18 sample may be attributed to the highly distributed MMA segments in PE leading to a high degree of disorder (DOD = 54.65).
4. The low mechanical properties of EMMA38 may be explained by its contribution coming mainly from the shorter chain segments leading to a lower T_c than EMMA18.
5. Intersecting the two compensation points found in the graph of entropy against enthalpy can be used to calculate the most probable glass-transition point of polymer. The result calculated for EMMA18 is −35.0 °C, while T_g for EMMA38 is −31.3 °C.

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