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Dynamic Mechanical Analysis of the Glass Transition: Curve Resolving Applied to Polymers

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ABSTRACT: This study attempts to apply techniques common to spectroscopy to clarify the contribution of various effects to the shape of the glass transition as measured by dynamic mechanical spectroscopy. Spectra of the tan δ as a function of temperature are fitted to Gaussian/Lorentzian functions, and the contribution of each line shape is determined. The known influences of crystallinity and molecular weight on T_g are reexamined using the curve-fitting approach, which leads to the identification of amorphous and crystalline-dominated T_gs in nylon-6. This new method of analysis is then extended to explain the differences observed in the mechanical relaxation spectra of the α- and γ-crystalline conformations of nylon-6.

Introduction

The transition of polymeric materials from the glassy state to the rubbery state has long been recognized as an important material property. Because of the dramatic changes that occur during this transition, this glass transition temperature, T_g, can be observed by many means, including dilatometry, dielectric and thermal measurements, and dynamic mechanical spectroscopy (DMS). Despite the ease of measurement of these properties, there is no satisfactory theoretical basis explaining the line shape of the loss tangent (tan δ) spectrum although many influences are partially understood.[1] The occurrence of multiple processes and thus the existence of multiple peaks in this region have not been completely accepted. Multiple glass transitions are accepted for certain types of copolymers, yet their appearance in homopolymer samples has been more difficult to explain. Multiple transitions have been postulated to occur due to segmental cooperation of domain sizes above and below the critical entanglement molecular weight,[2] copolymer compositional variances,[3] and the simultaneous presence of more than one crystalline form in the sample.[4]

The clarification of these issues would be aided by the development of a better understanding of the nature of the dynamic mechanical spectrum. In spectroscopy, the separation of overlapped bands can be accomplished through the use of curve-fitting techniques. The validity of resolving such individual band contributions is usually supported by evidence for a particular line shape. There is currently little such theoretical support for any specific line shape to appear in the dynamic mechanical spectrum of polymers when plotted as a function of temperature. It is possible, though, that the judicious use of curve-fitting analysis with a flexibility of line shapes may help to develop an improved comprehension of individual process contributions to the overall glass transition as observed by dynamic mechanical experiments.

Although the glass transition is associated with changes occurring in the disordered regions of the polymer, the effect of crystallinity on this transition is well documented. The effect of molecular weight has also been demonstrated, and methods of calculating the dynamic mechanical spectrum of samples with a bimodal molecular weight distribution have been developed.[5,6] The blending of two dissimilar polymers has been monitored by observing the glass transition region. The complete merger of individual component transitions may be observed for cases of completely miscible materials. It is not known whether the individual components could still be resolved from this merged glass transition, or if indeed their separation should be expected. A fuller understanding of each of these phenomena can be obtained by examining the frequency dependence of the dynamic mechanical spectra. The use of dynamic mechanical spectroscopy (DMS) has become popular due to the wealth of information available from one instrument, the ease of operation in comparison to dilatometry, and its sensitivity advantage over DSC measurements.[7] Unfortunately, double T_gs, which are apparent at the lowest frequency typical of DMS, 0.1 rad/s, often coalesce into a single peak at higher frequencies, making determinations of activation energies difficult. The use of curve-fitting procedures may thus be able to add to the knowledge which can be gleaned from DMS spectra by extending the range of frequencies where two or more processes can be separated qualitatively.

To this end, the spectra of several amorphous and semicrystalline materials have been measured. Curve-fitting routines have been used to analyze these dynamic mechanical spectra as well as data taken from the literature. While physical or theoretical interpretation of the line shape is beyond the scope of this paper, it is intended to observe any systematic trend without instrumental artifacts in order to examine the validity of curve resolving in dynamic mechanical analysis. The effects of well-understood variables such as molecular weight and crystallinity are now reexamined using the curve-fitting process both to test the technique and to gain new insights. This new analysis method is then applied to study influences on the glass transition which are not as well understood, specifically the differences in the glass transition of the α- and γ-crystalline conformations of nylon-6. It should be mentioned that a tan δ peak is not a glass transition temperature in a rigorous sense; it is nonetheless often used in the literature instead of loss modulus, G''. Sometimes, it is difficult to observe the G'' peak. For this reason, we used the tan δ curve for most of our study. The advantage of using the tan δ curve is that its behavior is independent of the sample geometry. We have also examined the applicability of our approach to G'' curves in limited cases.

Experimental Section

Several types of semicrystalline and amorphous polymers were used to study the applicability of the curve-resolving technique. These samples were compression molded using a 30 metric ton Carver press equipped with automatic pressure and tempera-

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Table I
Amorphous and Semicrystalline Polymers Used in This Study

polymer	description	mold temp, °C	T_g, °C
nylon-6	M_n = 6000, PDI = 1.8	240	64
nylon-12	Scientific Polymer Products, log no. 5	230	48
poly(butylene terephthalate)	General Electric, VALOX	240	80
polycarbonate	Dow Chemical, flow index = 10		160
poly(methyl methacrylate)	Polysciences, log no. 54,586, η = 0.2	160	130
poly(oxymethylene)	Scientific Polymer Products, log no. 3	190	140
poly(phenylene sulfide)	Phillips PR-10, no. 8060100, M_w = 15 000–60 000	315	108
poly(vinyl acetate)	polysciences, log no. 54,129, M_w = 90 000	160	51
poly(vinyl chloride)	BFGoodrich, Geon 86, η = 0.68	205	83
poly(vinylidene fluoride)	Du Pont	210	55
styrene–acrylonitrile	72.4% styrene, M_n = 100 000, PDI = 2	230	117

Table II
Molecular Weights of the Polystyrenes Used in This Study

nominal		measd before molding		measd after molding	
M	lot no.	M_w	PDI	M_w	PDI
4 000	86,597	4 460	1.07	4 430	1.08
20 000	86,599	20 900	1.07	20 200	1.16
30 000	91,610	29 600	1.08	28 900	1.08
50 000	90,984	45 900	1.10	45 700	1.18
120 000	86,600	115 000	1.16	110 000	1.16
400 000	83,438	358 000	1.43	133 000	5.95

ture control. This machine features variable cooling media dependent on the temperature range selected. A force of 2000 N was applied for 10 min after an initial 2-min heating at contact pressure. The processing temperatures are presented in Table I along with the temperature of the observed main tan δ peak. Samples were cooled to room temperature under pressure using the machine's automatic cooling device. Typical cooling time was 15 min. The poly(vinyl chloride) and poly(vinylidene fluoride) samples were observed to discolor slightly during the molding operation. The polycarbonate sample was received in the form of a molded plaque and was not remolded. The nylon-6 samples were originally prepared by the reactive molding of ε-caprolactam and recast for this study. This broad distribution of polymer types is helpful in developing an empirical basis for the analysis by line shape.

Dynamic mechanical specimens were cut from the molded plaques for analysis by a Rheometrics RMS-800 spectrometer. This machine has a temperature capability from −150 to +600 °C and a frequency range from 0.1 to 100 rad/s. A rectangular torsion test geometry was used with typical sample dimensions of 50 mm × 12 mm and a thickness of 1 or 3 mm. Temperature measurements were made bracketing the expected tan δ peak by 50 °C at a frequency of 1 Hz. For other samples, frequency–temperature sweeps were made covering frequencies of 0.1, 1.0, 10, and 100 rad/s. A strain sweep of each sample was performed to ensure that the measurements fell within the linear viscoelastic region.

To evaluate the effect of molecular weight, anionically polymerized atactic polystyrene samples were obtained in narrow molecular weight fractions from Polysciences Inc. The nominal molecular weight distributions of the samples used are shown in Table II along with measured values of the distribution before and after the molding process. Each sample was examined by gel permeation chromatography (GPC) to confirm the stated distribution and to examine the effect of molding. A Waters GPC was calibrated with polystyrene standards, and three columns (100, 50, and 10 nm) were used in series to achieve separation. Polystyrene samples were dissolved in tetrahydrofuran (THF) and filtered prior to injection into the column. The flow rate of THF carrier solvent was 1.0 mL/min, and the UV detector was tuned to 254 nm.

The polystyrene samples were prepared for dynamic mechanical analysis by an open molding process. A mold base and walls were created by wrapping a glass slide and metal bars in aluminum foil. This open trough was filled with polystyrene powder or melted pellets and placed into a small tubular dryer with a $CaSO_4$ present as a drying agent. The interior was heated by means of a conductive tape wrapped around the glassware. The dryer was evacuated for 1 min prior to heating to 200 °C. After the sample had melted, the chamber was backfilled with argon gas and cooled to room temperature over the course of 30 min. The use of argon pressures greater than atmospheric helped to prevent the formation of voids in the final mechanical specimen. For blended samples, reduced pressures were not employed to prevent possible disproportionate losses of the low molecular weight component by vaporization.

The lowest molecular weight sample of polystyrene required a more delicate molding procedure due to its extremely brittle nature. For this sample, M = 4000, and all subsequent blends, a silicone rubber mold was prepared using RTV 700 silicone rubber compound and Betal curing agent from General Electric Co. The better match of this organic mold's thermal expansion coefficient with that of the sample was necessary to prevent the initiation of cracks in the product upon cooling.

Initial blends were made by breaking the monodisperse DMS samples into chunks of approximately 0.05 g. These were then placed in the RTV mold in 3:1 and 1:3 ratios of high and low molecular weight. These materials were heated to 200 °C for 30 min and then cooled as before to generate samples of poorly blended molecular weight fractions. After dynamic mechanical analysis, each sample was broken up, remixed, and remelted for longer times to improve the homogeneity of the molecular weight distribution. In this manner, the 4000 molecular weight fraction was blended with the 400 000 molecular weight fraction.

The polystyrene samples were examined from 40 to 160 °C at intervals of 2 °C at a frequency of 1 Hz. An automatic strain adjustment was employed to keep the torque levels within the range of the transducer as the sample passed through its glass transition. An upper limit for the strain adjustment was determined from strain sweeps made to ensure that all measurements remained in the linear viscoelastic region.

Nylon-6 samples were cut from a single plaque and treated to obtain desired conformations. Samples with different levels of crystallinity were prepared by quenching and annealing. One bar was melted inside an open RTV mold and then quenched by sudden immersion in cold water. A second sample was annealed at 175 °C for 16 h under vacuum. Crystallinity was then calculated using aqueous solutions of CsI and a Gay-Lussac specific gravity bottle to measure the density of each sample bar. The density of the pure mesomorphous conformation was taken as 1.084 g/cm^3,[8] and those of each crystal form, 1.235 (α crystal) and 1.163 g/cm^3 (γ crystal), were taken from Table II.16 in Wunderlich's text,[9] where original references are cited.

A sample containing the γ-crystalline conformation was prepared following the method of Kinoshita.[10] The treatment bath consisted of 8.4 g of KI and 20 g of I_2 dissolved in 120 mL of deionized water. The rinse solution was prepared by dissolving 12.0 g of $Na_2S_2O_4$ in 120 mL of deionized water. An α-crystalline sample of 1-mm thickness was submerged in the treatment bath for 3 h and then transferred to the rinse bath for 3 days to produce the γ form. This sample was then rinsed with deionized water and allowed to dry at room temperature. A control sample was placed in deionized water for an equal amount of time during the treatment process.

Nylon-6 samples were examined over three frequency decades from 0 to 180 °C, then dried under vacuum at 60 °C for 2 days to reduce moisture, and reanalyzed. The dynamic mechanical data were then transferred to a Digital Equipment Corp. MicroVAX II computer running the VMS 5.3 operating system for analysis using an extensive in-house library of programs developed for spectral analysis. The curve-fitting routine employed uses a mixture of Gaussian and Lorentzian line shapes to achieve the best fit to the original spectrum based on a least-squares criterion. An analysis of spectra using an earlier version of this routine featuring strictly Lorentzian line shapes has been previously described.[8] This program allows the user to suggest interactively initial peak locations as well as the initial fraction of Gaussian

Table III
Results of Curve-Fitting Routines for Various Polymers

polymer	peaks, °C			% Gaussian	Σ squares
nylon-6	60	79	110	100	0.0002
nylon-12	41	51	79	91	0.0000
poly(butylene terephthalate)	74	87	107	100	0.0002
polycarbonate	156	162	168	100	0.0117
		163	169	70	0.0245
		163		48	0.1370
poly(methyl methacrylate)	128	131		89	0.0109
poly(phenylene sulfide)	99	113	137	100	0.0284
poly(vinyl acetate)	49	52	57	73	0.0002
poly(vinylidene fluoride)	55	70		100	0.0001
styrene–acrylonitrile	116	121		100	0.0205

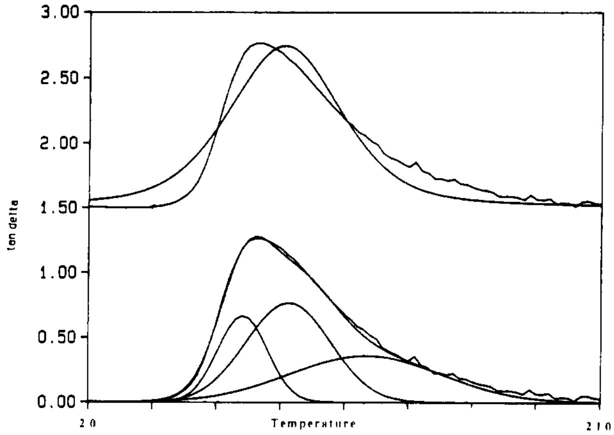

Figure 1. Curve fitting applied to the poly(phenylene sulfide) glass transition using one peak (top view) and three peaks (bottom view) with calculated summation.

character. In all cases a fit was attempted using a single peak and then using as many as three peaks. An initial guess of 50% Lorentzian and 50% Gaussian character was chosen for all attempts. Quality of fit could be examined by a visual comparison of the original spectrum with the best fit summation or numerically by analysis of the sum of squared differences.

Results and Discussion

The tan δ spectra of several different polymers were examined using the curve resolution technique. It was generally observed that the fit of a single symmetric peak to the glass transition was not of acceptable quality. An adequate fit was obtained with two or three peaks as is demonstrated in Table III and shown in Figure 1 for poly(phenylene sulfide). The value for tan δ is shifted for clarity. The values reported in Table III are for samples analyzed at either 1.0 or 6.28 rad/s, and the summation of squares of the residuals is included for comparison of three trials using polycarbonate. It is recognized that, as expected, the "goodness of fit" tends to improve monotonically with the addition of more peaks. However, it was observed in several cases that the contribution of an additional peak was vanishingly small compared to the previous best fit. In addition, by its very nature, the glass transition peak is not expected to be symmetrical, so the fitting of symmetric line shapes may be viewed as having limited utility. The emphasis of this study will be placed on the glassy side of the transition and on materials with a rubbery plateau where the effects of asymmetry are less pronounced. A more detailed summary of the line shape parameters, including full width at half-height (fwhh) and intensity for some of these curve fits, is presented in Table IV. The manifestation of very broad and shallow contributions may signal instances where symmetry considerations have adversely affected the results.

Table IV
Examples of Line-Shape Parameters for Selected Polymers

polymer	peak position, °C	fwhh, °C	intensity	% Gaussian
nylon-12	40.8	16.8	0.02	91
	50.6	33.0	0.10	
	78.9	35.0	0.01	
poly(butylene terephthalate)	74.2	14.0	0.06	100
	86.8	24.8	0.07	
	107.3	45.5	0.02	
polycarbonate	156.4	4.9	0.16	100
	162.5	6.3	1.70	
	168.0	8.9	0.56	
polycarbonate	162.7	6.9	1.84	70
	169.0	8.1	0.40	
polycarbonate	163.2	8.1	1.89	48
poly(vinylidene fluoride)	54.7	23.3	0.08	100
	70.3	28.1	0.04	
styrene–acrylonitrile	116.2	8.3	2.02	100
	121.3	20.5	1.34	

The glass transition is best viewed as a continuum arising from the variation of many factors. The influence of one or more major factors has already been examined as discussed above and can be used to draw important conclusions. The effect of hole size has been used by Fuoss,[12] for instance, to explain the simultaneous plasticization and antiplasticization of PVC depending on whether the α or β transition is examined. The purpose of applying this technique is to identify such major influences on the glass transition, specifically in mixtures where the constituents are known or can be reasonably postulated, not to assign unequivocally a particular process to an individual "peak" in the overall transition.

Such assignments have been made, though, using a simple curve-fitting approach in the region of the β transition, by Chiorboli and Pizzoli[13] in analyzing poly(butylene isophthalate), although the nature of the symmetric line shape they used was not discussed. In addition, Nishi and co-workers[14] have applied curve fitting to plots of tan δ versus inverse temperature, without discussing their choice of abscissa. The physical significance of the high-temperature peak in Figure 1 for poly(phenylene sulfide) is doubtful; however, the concept of multiple glass transitions in such materials is not entirely new. Lipatov et al.[15] have proposed the appearance of a separate T_g due to the intermolecular entanglements created by the agglomeration of larger clusters of molecules, in addition to the normal entanglements present. This is similar to the explanation proposed by Kurata[2] and alluded to earlier.

Although there is scant evidence in the literature for any particular line shape,[16] it is interesting to note that in the analysis of a wide variety of polymers, the line shape resulting in the best fit turned out to be purely or almost purely Gaussian in form in almost every case. A spectrum composed entirely of Lorentzian peaks was generated as a control and successfully identified to be Lorentzian in shape by the curve-resolving program. The amount of Gaussian character attributed to this control could be viewed as a rough measure of the error in assignment of curve type. Data taken from the literature also were best fit by the Gaussian line shape, including samples run using the torsional braid,[17] torsion pendulum,[4] dielectric,[12] and dilatometer[18] analyses. A new thermally stimulated current technique being developed[19] was also found to result in a glass transition that was the sum of purely Gaussian processes. The loss modulus, G'', spectrum of the poly(phenylene sulfide) sample was also examined by curve fitting, and the components were found to be mostly Gaussian in character. These literature and control data are reported in Table V; the statistical and peak position

Table V
Results of Curve-Fitting Routines for the Data Obtained by Various Techniques Reported in the Literature

technique	% Gaussian	ref
dielectric measurement	100	12
dilatometry	100	18
thermally stimulated current spectroscopy	94	19
torsional braid analysis	100	17
torsion pendulum analysis	100	4
computer-generated Lorentzian control	8	
G'' of poly(phenylene sulfide)	86	

information is omitted since the wide variety of units makes comparisons meaningless. This empirical evidence suggests that this type of line shape is intrinsic to the relaxation processes themselves and not to the method of analysis or the chemistry of the polymer. The use of a Gaussian curve-fitting program has also been reported in the analysis of differential scanning calorimetry (DSC) experiments.[20] Differential scanning calorimetry can be used to observe the glass transition point although it is difficult to correlate the scanning rate with any particular frequency of mechanical analysis.

Molecular Weight Effects. The blending of the polystyrene molecular weight fractions is a classic experiment in dynamic mechanical spectroscopy. The glass transitions of the individual fractions followed the behavior qualitatively expected from the Flory–Fox equation. The lowest fraction, 4000 *M*, had a tan δ peak at 104 °C, and the 400 000 *M* sample had a tan δ peak at 119 °C. These values are slightly higher than accepted literature values. This result may be due to the use of free radical polymerized samples used by other groups which have been shown to exhibit a glass transition well below that of samples produced anionically.[21] The process of using the maximum of the tan δ curve in dynamic mechanical analysis can also be expected to give a higher value than many other techniques. Roe[22] has shown that the effective frequency of dilatometer experiments can be taken as $10^{-3.8}$ Hz. Using an apparent activation energy of 101.0 kcal/mol taken from Boyer,[23] who cites original references, one can calculate that the transition observed by Roe at 373 K for polystyrene corresponds to a T_g of 396 K (123 °C) in a dynamic mechanical spectrum scanned at 1 rad/s.

The important observations to be made here involve the shift in tan δ peak upon blending of components, not the absolute value. If two fractions are mechanically blended, Bersted[5] has shown that the resultant relaxation spectrum can be calculated based on the spectra of the individual components. His analysis is restricted to samples well above the critical entanglement molecular weight, M_c, and assumes good dispersion of the two components. Using the curve-fitting approach, it is possible to examine cases where one component is substantially below M_c and to observe the transition from an inhomogeneous to a homogeneous mixture.

This situation is analogous to the behavior of copolymers with incompatible blocks, which is more easily understood. For large domain sizes, two completely separate glass transitions may be observed depending on the "natural" location of each pure component T_g. The appearance of a separate T_g due to the interphase has been postulated[24] but shown not to be strictly required.[25] Thomason[26] has recently demonstrated that the use of scanning rates greater than 2.0 °C/min can lead to artifacts in the DMS spectrum which may be misinterpreted as evidence for an interlayer. As the block length decreases, one component will not be able to form domains large enough to support the glass transition process, which is thought to involve the cooperative motion of 40–60 chain atoms.[16,27] The T_g of this component will seem to disappear or may simply broaden and shift as this block is incorporated into the interphase fraction. Eventually, on the scale of glass transition cooperative processes at least, a homogeneous dispersion of the two incompatible components is achieved which results in a single T_g at some position intermediate to the pure components. This has also been viewed as a blend with an interlayer volume fraction of unity.

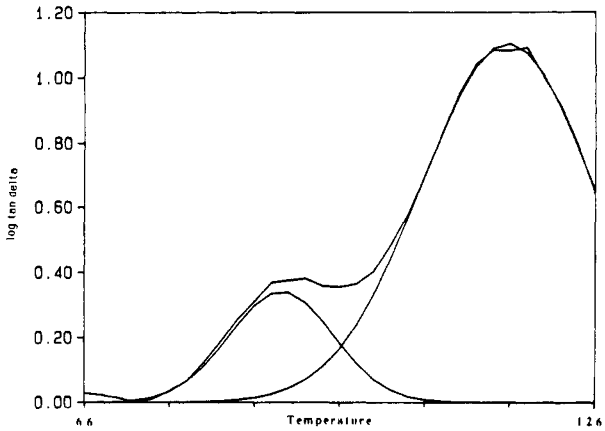

Figure 2. Curve fitting of the dynamic mechanical spectrum of poorly blended polystyrene molecular weight fractions. Mixture is 3:1 ratio of 400 000 *M* and 4000 *M* fractions having a polydispersity of 1.06.

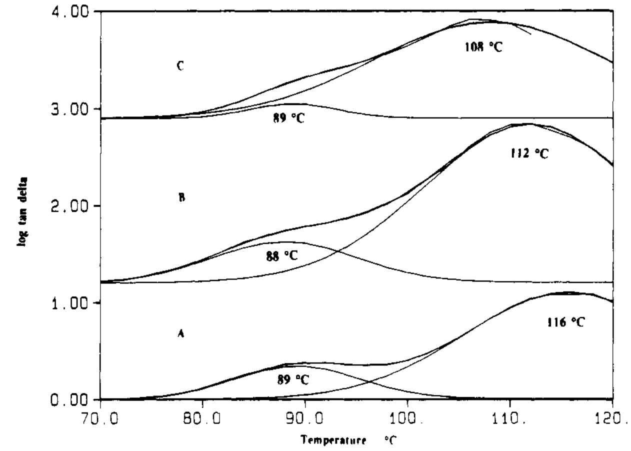

Figure 3. Glass transition region of polystyrene blends after heating to improve blend homogeneity: (A) initial sample; (B) heated for 3 h at 180 °C; (C) heated for 15 h.

In the mixing of two disparate molecular weight fractions, where the compatibility of the two components is excellent, it can be expected that the individual glass transitions may be completely merged. Such appears to be the case in the polystyrene data of Glandt et al.,[28] who investigated the T_{ll} transition above T_g by differential thermal analysis. They did postulate that this higher temperature transition could be fit by a superposition of the individual component T_{ll}s. A discontinuity in the plots at the glass transition prevents the same analysis of this region by any curve-fitting method. Separation of this region in blends of monodisperse fractions of polystyrene can be achieved, however, by physically creating domain sizes large enough to support individual glass transitions. The creation of such a poorly blended sample was described above, and its dynamic mechanical spectrum is displayed in Figure 2 with the results of a curve fit employing two peaks for comparison. Figure 3 shows the same material compared with mixtures featuring progressively better blending. The plots of logarithmic tan δ vs temperature are arbitrarily shifted along the ordinate axis to better illustrate the changes occurring. The coalescence of the two individual fraction T_gs is unmistakable. The high molecular weight component shifts to lower temperatures due to plasticization by the low molecular weight material.

It is puzzling to note that the transition appearing to result from the presence of the low molecular weight component in these spectra is located at a position some 10 °C below the tan δ peak of the pure 4000 M sample. Such behavior would indicate an increase in the mobility of the low molecular weight component or an apparent decrease in the molecular weight of this constituent. The presence of the high molecular weight material could enhance the mobility of the smaller species. The possibility of degradation of the low molecular weight species, due to the observed slight yellowing of the blended samples, has also been considered. However, the storage shear modulus, G', of the mixed samples is comparable in magnitude to that of the individual constituents and did not decrease upon further heating. In addition, GPC analysis showed only slight degradation of all the species except the highest molecular weight fraction. The molecular weight of this fraction was reduced from 400 000 to 135 000 upon molding, both of which however are at the limits of the column calibration.

Even if such a large drop occurs, the change in T_g of this component should be negligible. Toh and Funt[29] found that the thermal degradation of an 80 000 molecular weight sample of polystyrene without a stabilizer resulted in a total decrease in T_g of approximately 2 °C over 9 h at 313 °C under nitrogen. Kovacevic et al.[30] have reported that the thermal degradation of polystyrene takes place preferentially at the chain ends of high molecular weight species. Such a process would explain the considerable broadening of the molecular weight distribution and the fact that the apparent final T_g of the well-mixed binary mixture is much lower than that predicted by the Fox equation: $1/T_g = w_1/T_{g1} + w_2/T_{g2}$, where w_i is the weight fraction of component i with a glass transition temperature T_{gi}. The applicability of this equation to species below the critical entanglement molecular weight, M_c, is only of a qualitative nature though. M_c for polystyrene is usually taken as 37 000 in solution and may be as low as 10 000 in the melt state.[23]

While the curve-fitting method will not be used to make quantitative judgments based on the peak areas of each component, an interesting qualitative assessment can be made. The contribution of the low molecular weight component appears to decrease as the two transitions merge, even though the volume fractions remain constant. Thus, it can be concluded that the low molecular weight component becomes fully associated with the high molecular weight fraction before the latter is completely plasticized. Such behavior is not surprising when considering the volume fractions are in a ratio of 3:1 for 400 000 M: 4000 M and the greater mobility of the low molecular weight component.

In the curve analysis of the polystyrene blends, it may be expected that a third glass transition peak, representative of the interlayer phase, should be discernible. To investigate this possibility, the curve fitting was repeated with a third peak postulated to exist between the two visible transitions. In all cases, including samples run at 3.0 °C/min, the contribution of this third peak rapidly became negligible as the fit improved. It is likely that the inherent compatibility of the two components leads to an interphase which is not substantially different in relaxation behavior from one component. The absence of this interlayer peak supports the integrity of the curve-resolving process in that an extra parameter, even though there may be a vlid expectation of its existence, is not always needed to resolve the spectrum. A third peak might be revealed if an asymmetric line shape were used to resolve the spectrum, but it is doubtful that the positions of the two major glass transitions would not be affected.

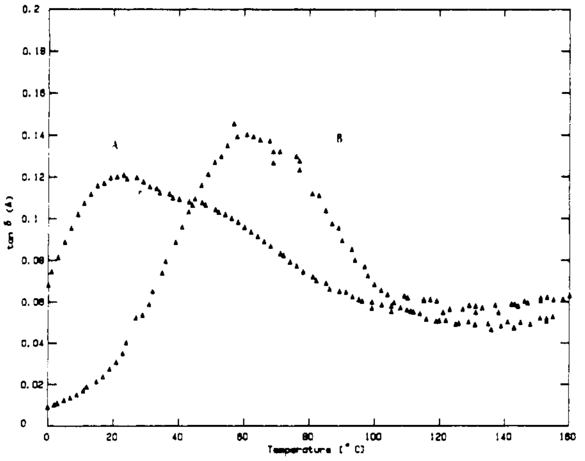

Figure 4. Dynamic mechanical spectra of nylon-6 before (A) and after (B) drying.

Crystallinity Effects. In the analysis of semicrystalline materials, it has been pointed out that much of the confusion over the glass transition arises because the T_β transition may be larger in intensity than T_g as high crystallinity is approached.[31] In nylon-6, the intensity of the transition is highly dependent on the water content of the sample and can thus be essentially removed by judicious drying techniques. Ning and Ishida[32] have examined dried nylon-6 samples and discovered a second β process at about −100 °C when measured at 1 Hz. This water-independent transition is too weak and distant to influence determination of the glass transition. The drying procedure used for these experiments successfully eliminated the contribution of the water-related transition to the nylon-6 relaxation spectrum as shown in Figure 4.

Although the glass transition is generally thought of as a process related only to the amorphous component of a semicrystalline polymer, it can also be related to morphologies common in highly crystalline regions. The presence of tie molecules, loose loops, cilia, and crystal defects can give rise to a glass transition. As such, it has been stated that a semicrystalline material should be treated as a composite with two T_gs. Boyer,[23] for example, has declared that the confusion over the location of the polyethylene T_g can be resolved by considering the amorphous T_g or T_g(l) to be at −80 °C and a separate crystalline-dominated T_g or T_g(u) to exist at −30 °C. Seferis[31] has suggested that there will be a statistical distribution of polymer lengths which are free to contribute to the glass transition. The shorter loops will give rise to the high-temperature portion of the glass transition. In semicrystalline polymers it can be expected that these short segments will be predominantly associated with the crystalline portion of the material. The inability of the smallest defects to support a T_g explains the apparent maxima in some literature plots of T_g vs crystallinity. In this case the average length of the loops which can contribute to the relaxation process is less than for samples of slightly lower crystallinity. Seferis did not postulate whether the expected distribution of loop lengths should be Gaussian.

The investigation of nylon-6 having different levels of crystallinity illustrates this double-T_g behavior. Dynamic

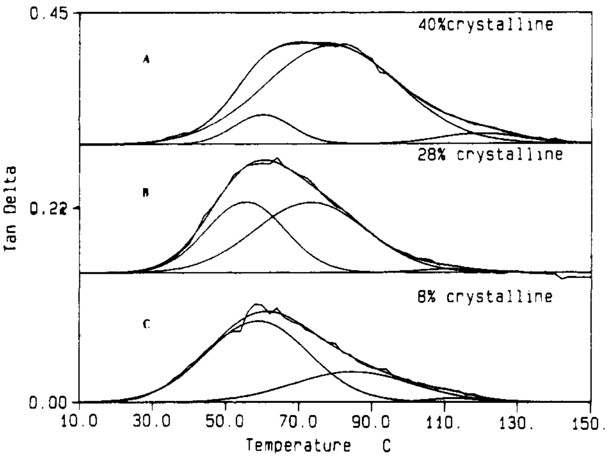

Figure 5. Dynamic mechanical spectra curve resolved for nylon-6 samples of 40% (A), 28% (B), and 8% (C) α crystallinity.

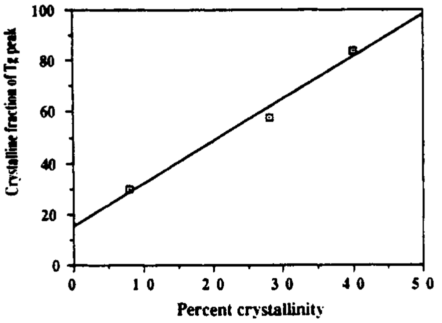

Figure 6. Plot of the fraction of T_g attributable to the crystalline-dominated portion vs bulk percent crystallinity.

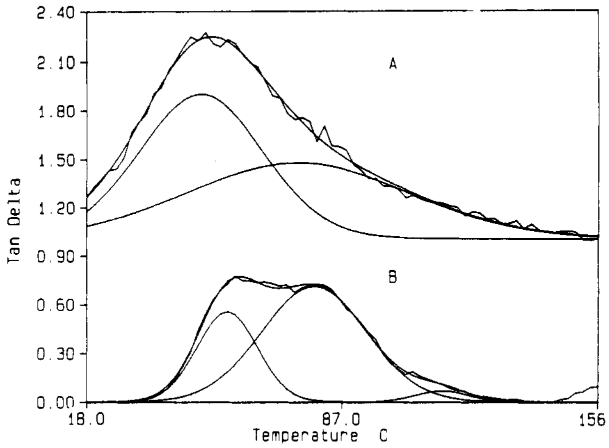

Figure 7. Dynamic mechanical spectra and related curve fittings of the α (A) and γ (B) forms of nylon-6.

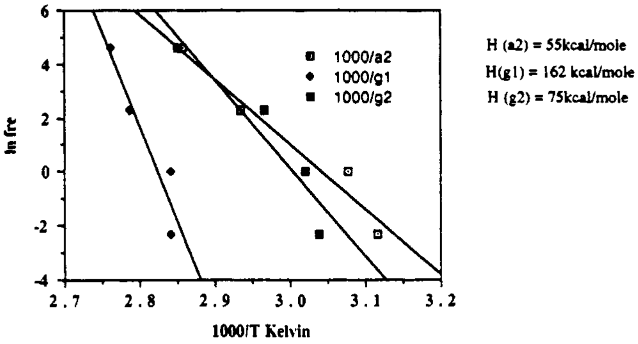

Figure 8. Arrhenius plot of α and γ nylon-6 glass transition processes.

mechanical spectra of nylon-6 samples of high and low crystallinities are plotted as tan δ versus temperature in Figure 5. In Figures 5 and 6, the ordinate value for tan δ is shifted for clarity. Curve fitting clearly highlights the growth of the fraction responsible for the high-temperature side of the transition. Using Boyer's hypothesis, this high-temperature component could be viewed as the crystal-dominated glass transition of nylon-6. The curves in Figure 5 then indicate an increase in the number of amorphous segments hindered by neighboring crystallites and perhaps crystalline perfection as annealing progresses. Thus growth of the high-temperature side of the glass transition is at the expense of the purely amorphous-component T_g. Figure 6 shows a linear relationship between the percentage of T_g(u) responsible for the T_g and the overall percent crystallinity. This relation may have resulted from a fortuitous effect of spherulite size and obviously fails at very low levels of crystallinity, yet presents an interesting case in which the intensity of part of the glass transition increases with crystallinity. Although this analysis does not explain the work of Northolt et al.,[33] who have found values of the nylon-6 T_g to exist from 22 to 190 °C depending on annealing conditions, it encompasses their explanation that T_g is influenced by the perfection of the hydrogen bonding. It is proposed that the nylon-6 glass transition is located at approximately 57 °C with a crystalline-dominated transition at 84 °C.

The dynamic mechanical spectra of the γ-crystalline form clearly show the existence of two processes at lower frequencies. The α-crystalline material shows strong evidence of only one major process. This is depicted in Figure 7, where samples containing each conformation were measured at a frequency of 0.1 Hz. The α-crystalline T_g occurs at a slightly lower temperature than that of the γ form, which may seem surprising since the latter form is thermodynamically less stable. Illers[34] has calculated the heat of fusion, ΔH_f, for each conformation and found them to be 241 J/g for the α form and 239 J/g for the γ form. However, the glass transition is actually affected by the strength of the hydrogen bonding of the amorphous phase and not the integrity of the crystal. Data compiled by Salem and Weigmann[35] on the unit cell dimensions of α and γ nylon-6 indicate that the hydrogen bond length in the γ form is the same if not slightly smaller than that in the α-crystalline form when variances in the β angle are considered. More importantly though, in the γ-crystalline conformation, a three-dimensional hydrogen-bonding network exists which can more closely interact with the neighboring amorphous segments. The hydrogen bonding in the α-crystalline phase is confined within the fold planes and thus it is not surprising to observe a weaker interaction with the amorphous regions. The appearance of the high shoulder peak in the γ-crystalline material can therefore be explained by the nature of the crystallization of each material. Amorphous regions constrained by the neighboring γ-crystalline zones can be expected to have a higher glass transition.

Conclusions

The curve resolution analysis of dynamic mechanical spectra has been used to evaluate the glass transition region of various polymers. The empirical validity of this approach has been demonstrated, and the Gaussian line shape has been suggested as being intrinsic to the nature of the components which constitute the spectrum. The use of the curve resolution technique has led to valuable qualitative insights to the blending of compatible polymers and the manifestation of crystallinity effects on the glass transition. The identification of a crystalline-dominated

T_g at 84 °C has been made for nylon-6. In addition, this technique has proven useful in explaining the existence of a secondary relaxation process in the study of γ-crystalline nylon-6. The activation energy of this process is in agreement with the expected increased interaction of this crystal form with neighboring amorphous material.

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Registry No. Nylon-6, 25038-54-4; nylon-12 (copolymer), 25038-74-8; nylon-12 (SRU), 24937-16-4; poly(butylene terephthalate) (copolymer), 26062-94-2; poly(butylene terephthalate) (SRU), 24968-12-5; poly(methyl methacrylate), 9011-14-7; poly(vinyl acetate), 9003-20-7; poly(vinylidene fluoride), 24937-79-9; styrene–acrylonitrile, 9003-54-7.