Synthesis and Properties of Poly(vinyl chloride-*co*-trimethylolpropane monoallylether)

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ABSTRACT: A thermally stable, high molecular weight copolymer of vinyl chloride and trimethylolpropane monoallylether (PVC-*co*-TMPME) has been synthesized via the suspension polymerization process. Proton nuclear magnetic resonance (NMR) characterization of the copolymer shows the presence of TMPME in the saturated form, indicative of the TMPME reaction. Characterization by differential scanning calorimetry (DSC) shows that the glass transition temperature of the TMPME copolymer is similar to that of the homopolymer, and to that of a 5% vinyl acetate (PVC-*co*-VA) copolymer. Characterization of plasticized polymers by dynamic mechanical analysis (DMA) shows that both PVC-*co*-TMPME and PVC-*co*-VA have lower modulae than the corresponding homopolymer, as well as lower distortion temperatures, as shown by creep compliance master curves. These data indicate that PVC-*co*-TMPME should share similar process and end-use property characteristics with conventional PVC copolymers without adversely affecting thermal stability. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1603–1612, 1997

Key words: poly(vinyl chloride); trimethylolpropane monoallylether; NMR; modulus; thermal stability; creep compliance

INTRODUCTION

The physical properties of copolymers are typically hybrids of each homopolymer component. For example, it is well accepted that styrene–butadiene–styrene (SBS) triblock copolymers possess the low-temperature flexibility of polybutadiene, while maintaining the higher distortion temperature of the higher glass transition temperature (T_g) component, polystyrene.[1] Similarly, random copolymers of vinyl chloride (VC) and vinyl acetate (VA) exhibit glass transition temperatures between those of pure VC and VA homopolymers. Also, the presence of VA comonomer, even at low concentrations, results in a significant reduction in melt viscosity, and hence, a reduction in process temperature.[2]

Plasticized PVC homopolymers exhibit a morphology that is dependent on process history,[3,4] molecular weight,[2] tacticity,[5] and plasticizer solubility.[6,7] In all cases, the morphology can be generally described as heterogeneous with microscopic domains of high and low plasticizer concentrations. The microscopic domains of low plasticizer concentration provide the macroscopic system with physical crosslinks, and hence, with elastomeric characteristics akin to those found in SBS triblock copolymers. Typical thermoforming process temperatures for plasticized PVC range from about 160 to 190°C, depending on the type and level of plasticizer. These high process temperatures are a consequence of the "rigidity" of the unplasticized domains. The low concentration of plasticizer in these domains creates the need for high temperatures to activate the molecular motion that precedes chain disentanglement—a prerequisite for the thermoforming process.

The VA sequences in PVC/VA copolymers dis-

rupt the tendency for the highly polar VC sequences to form intermolecular associations in the solid state, thereby decreasing the temperature required for chain disentanglement.[8] Thus, the introduction of VA comonomer into the PVC backbone structure results in a lower melt viscosity, and in a lower thermoforming process temperature, both of which depend on the level of comonomer employed. Thus, if a lower process temperature is desired together with physical properties that are closely matched to PVC homopolymer, a small amount of comonomer can have a significant effect. Unfortunately, however, the thermal stability can be adversely affected, particularly when VA is incorporated as the comonomer.

The thermally activated dehydrochlorination of PVC has been a subject of extensive review in the literature.[9–11] Although controversy still exists over the exact mechanisms of degradation and stabilization, it is generally understood that primary group IIa and IIb metal salts with alkyl organic ester ligands have profound and often synergistic stabilizing abilities. The most important of the group IIb metals is Zn, which provides early color retention during high temperature static oven degradation tests, particularly when it is used in combination with a group IIa metal such as Ca or Ba. It is thought that the higher covalent character of the Zn/ester linkage is critically related to the efficiency of ligand transfer to allylic Cl defect sites on the main polymer chain.[12]

The majority of allylic defect sites occur at the ends of polyene sequences, which are formed as a result of thermally activated steplike dehydrohalogenation, or "unzipping." The length of the polyene sequence determines its extinction coefficient and maximum absorbance wavelength. Generally, when the polyene chain length reaches about five units, visible color can be observed.[13] The transfer of ligands from the metal stabilizers can reduce the conjugation length, and hence, can shift the absorption maximum from the visible to the ultraviolet region, thereby imparting "color retention." The byproduct of this reaction is $ZnCl_2$, which behaves as a Lewis acid and actually accelerates the dehydrochlorination process. Thus, secondary additives are often employed for the purpose of reducing the Lewis acidity of $ZnCl_2$ through chelation. Examples of secondary additives that are used for this purpose include β-diketones, α-phenylindole, and polyhydric alcohols such as pentaerythritol and trimethylolpropane.[9,12]

Given that the thermal stability of PVC-*co*-VA is generally worse than the PVC homopolymer, other copolymers have been developed in an attempt to achieve a low temperature processing resin without influencing thermal stability. Many examples exist, including PVC copolymerized with olefins, acrylates, and vinyl ethers.[2] However, the thermal stability is usually worse than PVC homopolymer unless the comonomer level surpasses the VC level. Unfortunately, at that point the physical properties begin to resemble those of the second component as opposed to PVC.

Thus, the problem remains to find a comonomer that can be used at low levels so that process temperatures can be decreased, while simultaneously maintaining PVC homopolymerlike properties at end-use temperatures—without disrupting thermal stability. To reach this end we have proposed to incorporate a functional group that is known to improve thermal stability, trimethylolpropane,[9,12] through the polymerization of trimethylolpropane monoallylether (TMPME) with a VC monomer to yield a polymer with a lower processing temperature than the PVC homopolymer, and with improved thermal stability. The initial results of this study are presented in this article.

EXPERIMENTAL

Polymerization

Poly(vinyl chloride), having a number-average degree of polymerization of 1000, was obtained from the Shintech Company, under the trade name SE1000. A poly(vinyl chloride-*co*-vinyl acetate) (PVC-*co*-VA) polymer containing approximately 5% VA by weight was obtained from Vygen (V255, degree of polymerization of 1000). A copolymer of VC with TMPME was prepared via a batch suspension process, where a suspension reactor was charged with monomers, deionized water, catalysts, and surfactants at the following levels, expressed in parts per hundred monomer (phm): VC monomer (Vista), 100; deionized water, 145; Lup 10 (*t*-butyl peroxyneodecanoate, Elf Atochem), 0.03; Lup 688 (1,1-dimethyl-3-hydroxybutyl peroxyneoheptanoate, Elf Atochem), 0.03; poly(vinyl alcohol) (72% —OH, Air Products), 0.04; poly(vinyl alcohol) (55% —OH, Air Products), 0.09; TMPME (Perstorp Polyols, Inc.), 3.0.

The reactor was first charged with water and surfactant, and was then charged with VC monomer together with TMPME monomer. The sus-

pension was then heated to a temperature of 53°C under vacuum, at which time the catalysts were charged. The polymerizations were stopped at the point where a 10 psi pressure drop was recorded from the initial pressure at 53°C. The resultant slurry was then "stripped" by water washing for 10 min with centrifugal separation at 85°C. The resin was then cooled to 62°C where it was maintained until completely dry. A sample of "unstripped" resin was also collected and dried separately for analytical comparison to the "stripped" resin.

The resins were tested for relative molecular weight by inherent viscosity using ASTM D1243–66. The inherent viscosities of SE1000, V255, and PVC-*co*-TMPME were 0.93, 1.02, and 0.95, respectively.

Formulation Processing

SE1000, V255, and "stripped" PVC-*co*-TMPME were each dry mixed with plasticizers and thermal stabilizers at room temperature prior to milling for 5 min at 330°F on a Brabender two roll mill. The following formulation was used for each resin with all ingredients expressed in parts per hundred resin (phr): Resin, 100; di-2-ethyl-hexylphthalate (DOP, Aldrich), 45; Epon 828 epoxy (Shell), 5; Thermchek 130 (Ba/Zn stabilizer, Ferro), 3.

NMR Analysis

Proton NMR spectra were obtained for PVC-*co*-TMPME resin both before and after complete stripping to determine the fraction of reacted TMPME. The unstripped resin was subjected to the same drying procedure as the stripped resin prior to NMR analysis. All NMR spectra were acquired on a General Electric GN300 NMR spectrometer operating at a resonance frequency of 300.1 MHz for ^{1}H. The spectra were acquired as solutions in tetrahydrofuran-d8 (5% by weight polymer) as the analytical solvent. All proton spectra were acquired with sufficient relaxation delays to insure that the resulting spectra were quantitative. Each spectrum was obtained using a 20° proton pulse, a 10-s recycle delay, and with signal averaging of 128 scans. Integrations of proton peak areas were used to quantify the mol fraction of each proton type, which could then be converted to molar equivalents of VC monomeric units, of reacted TMPME monomeric units, and of unreacted TMPME monomer. These molar
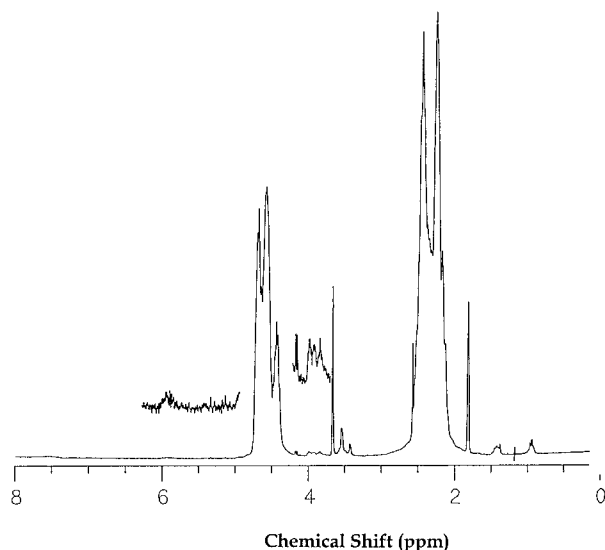
Figure 1 Proton NMR spectra and structural peak assignments for "stripped" PVC-*co*-TMPME. Residual allylic monomer was below the detection limit. The weight percent of reacted TMPME monomer was determined to be 1.9% by weight from integrated intensities.

equivalents were then converted to weight percents by accounting for the molar molecular weight of each monomeric species (62.5 amu and 174.2 amu for VC and TMPME, respectively). The composition of the polymer system with residual TMPME monomer was found by normalizing the data to remove the monomer weight. The reproducibility was determined to be ±0.1 wt % for each measured attribute.

The proton spectra of the stripped and unstripped PVC-*co*-TMPME are shown in Figures 1 and 2. Peak assignments and chemical structures are provided in Table I.

The composition was quantified by using integrated peak areas as follows: A = area of PVC methine proton #1 = (area from 4.1 to 4.8 ppm)/1; B = area of monomeric TMPME allylic methylenes #8 = (area from 5.0 to 5.3 ppm)/2; C = area of poly TMPME methylenes #3, and #4 = [(area at 3.4 ppm + area at 3.48 ppm) − (6B)]/6; mol % PVC = A/(A + B + C); mol % monomeric TMPME = B/(A + B + C); mol % poly TMPME = C/(A + B + C).

Thermal Analysis

The plasticized milled samples were analyzed for relative creep compliance behavior using the capabilities of the TA Instruments 983 DMA and time−temperature superposition software. Each
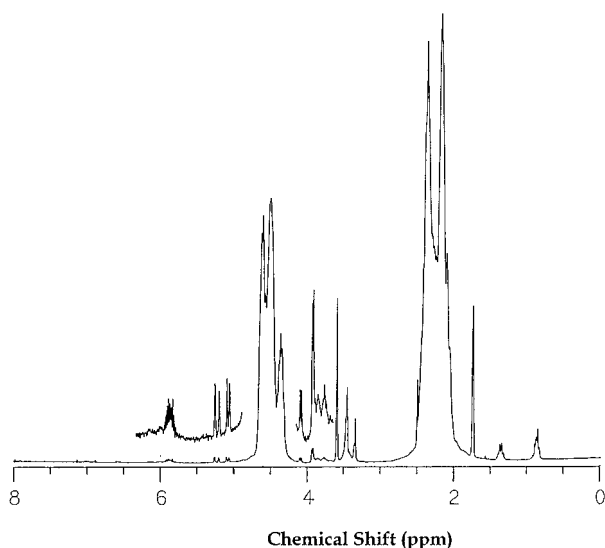
Figure 2   Proton NMR spectra and structural peak assignments for "unstripped" PVC-*co*-TMPME. The weight percents of residual allylic TMPME and reacted TMPME were determined to be 0.5 and 1.9%, respectively, from integrated intensities.

sample was subjected to a common thermal history prior to analysis with a common time–temperature profile. The PVC and copolymer samples were vertically suspended for 5 min in the machine draw direction in an oven set at 155°C. This step was required to reduce the residual shrinkage stresses from the process history of the films so that relative DMA measurements could be made. Samples were mounted in the DMA instrument in the vertical mode with the stress being applied transverse to the machine draw of the plastic. The sample thickness ranged from 1.20 to 1.65 mm, with a width of approximately 15 mm,

and with a length of approximately 5.5 mm between the DMA clamps. These sample dimensions were found to be optimum for producing the least amount of sample distortion over the broad range of temperatures that were required for the measurements.

Samples were clamped with a torque of 8 inch-pounds, and the sample arms were adjusted to the zero position prior to beginning a preprogrammed multiplex run. Samples were equilibrated at 35°C, and were then subjected to a constant stress (at an initial displacement of 1.0 mm) for 1.5 min of creep. The stress was then removed, and the samples were heated by an additional 7°C increment, and the stress was reapplied. These segments were repeated at 7°C increments up to a temperature of 190°C. Master curves of shear $(J(t))$ creep compliance were constructed with the TA instruments time–temperature superposition software using a segment at intermediate temperatures as the reference temperature. The resultant master curves were then referenced to 150°C for relative comparison.

The TA Instruments 983 DMA was also used to analyze the plasticized milled samples in fixed frequency mode. The samples were oscillated at 1 Hz and 0.4 mm amplitude in vertical mode. The samples were cooled to −150°C, and were then heated to 70°C at a rate of 5°C/min. Storage modulae (E' GPa) and loss modulae (E'' MPa) were plotted as a function of temperature.

A TA Instruments 910 DSC (differential scanning calorimeter) was used to measure the relative glass transition of the neat resins (T_g). Approximately 7 mg of each sample was weighed into aluminum pans with lids. Sample pans were run with an empty pan as a reference under dry

Table I   PVC-*co*-TMPME Polymer, and Allylic TMPME Monomer Proton NMR Peak Assignments with Chemical Structures

Proton Number	Chemical Shift (ppm)	Structural Identification
1	triplet, 4.1–4.8	PVC methine
2	doublet, 1.9–2.6	PVC methylene
3	singlet, 3.48	TMPME methylene
4	singlet, 3.4	TMPME methylene
5	quartet, 1.4	TMPME methylene
6	triplet, 0.9	TMPME methyl
7	doublet, 3.9	TMPME allyl ether methylene
8	multiplet, 5–5.3	TMPME allylic methylene
9	multiplet, 5.8–6	TMPME allylic methine
10	3.58, 1.8	residual THF

nitrogen. Samples were cycled twice between −100 and 100°C at a rate of 10°C/min. The first run was used to establish a common thermal history, whereas the second run was used to compare glass transition values. T_g was reported as the onset temperature of the apparent second-order transition from the heat flow (W/mg) versus temperature curves.

Static Oven Stability

Plasticized resin samples were heated in a forced air oven at temperatures of 170 and 180°C. Sample plaques of $1 \times 1 \times 0.020''$ were placed in the oven at 180°C (±1°C) and were removed at 10-min intervals up to a total time of 100 min, the time for the last sample to turn black. Similarly, sample plaques of $1 \times 1 \times 0.020''$ were placed in the oven at 170°C (±1°C) and were removed at 20-min intervals up to a total time of 200 min, the time for the last sample to turn black. The time interval at which blackening occurred was reported for each sample at both temperatures.

RESULTS AND DISCUSSION

Characterization of PVC-*co*-TMPME

The NMR spectra in Figures 1 and 2 show the presence of both vinyl chloride protons (the large, broad peaks) as well as protons from the TMPME functionality. The scale for the TMPME peaks is expanded in both spectra to illustrate the differences between the two samples. Namely, the unreacted TMPME in the "unstripped" resin is characterized by the presence of allylic vinyl protons at 5.0 to 5.3 ppm (all peak assignments are provided in Table I). The allylic resonances are absent in the "stripped" resin, which indicates that a portion of the allylic monomer has reacted during the vinyl polymerization.

Integration of the relative VC and TMPME peaks (both reacted and residual allylic TMPME) shows that the "stripped" resin contains 1.9% of poly TMPME by weight with no residual monomer, whereas the "unstripped" resin contains 1.9% poly TMPME by weight, and 0.5% residual monomer. Hence, the overall TMPME reaction efficiency under the conditions of the free radical suspension polymerization is approximately 63%. On the other hand, the relatively high inherent viscosity (0.95) indicates that the entire reaction reached a high degree of conversion, which is surprising given the autoinhibition tendency of allylic monomers.[1,14]

Chain transfer termination through abstraction of the α-hydrogen prevents high conversion during homopolymerization of allylic monomers, and also can limit the degree of conversion in free radical copolymerizations. The reactivity of TMPME is also influenced by the presence of oxygen,[14] as was shown for the case of styrene solution polymerizations in toluene, where TMPME was observed to form peroxides that retarded the onset of the polymerization. Furthermore, TMPME did not form a copolymer with styrene monomer under solution polymerization conditions.

Unlike prior results with styrene monomer, it appears that the TMPME can form a copolymer with vinyl chloride. The difference between the styrene and VC copolymerizations with TMPME could be strictly related to differences in reactivity ratios between the two sets of monomers.[1] However, it is also likely that the efficiency of the copolymerization reaction depends on the mode of polymerization. For example, the mechanism of suspension polymerization differs greatly from homogeneous polymerizations in that water is the continuous phase, and suspended monomer droplets are the reservoirs for the polymerization process. Under these conditions, the solubility of the monomers in water can have a substantial effect on reaction rates, and on comonomer sequence distribution. The initiator in the suspension process is "oil soluble," which implies that the bulk of the initiation occurs in the monomer droplets. The high hydroxyl content of TMPME renders it more water soluble than vinyl chloride monomer. This may minimize the concentration of TMPME in both the VC monomer droplets and in the resultant PVC particles, which would minimize both the probability of retardation, and the probability of chain transfer termination. Thus, although higher levels of TMPME would probably augment the termination rate and minimize the resultant molecular weight, it appears that the level used in this study (3%) has no adverse effect on molecular weight, and yields a copolymer containing 1.9% TMPME as shown by proton NMR.

Thermal Analysis of Homopolymer Versus Copolymers

DSC traces for PVC homopolymer, PVC-*co*-VA, and PVC-*co*-TMPME are shown in Figure 3. The glass transitions were taken from the onset of tan-
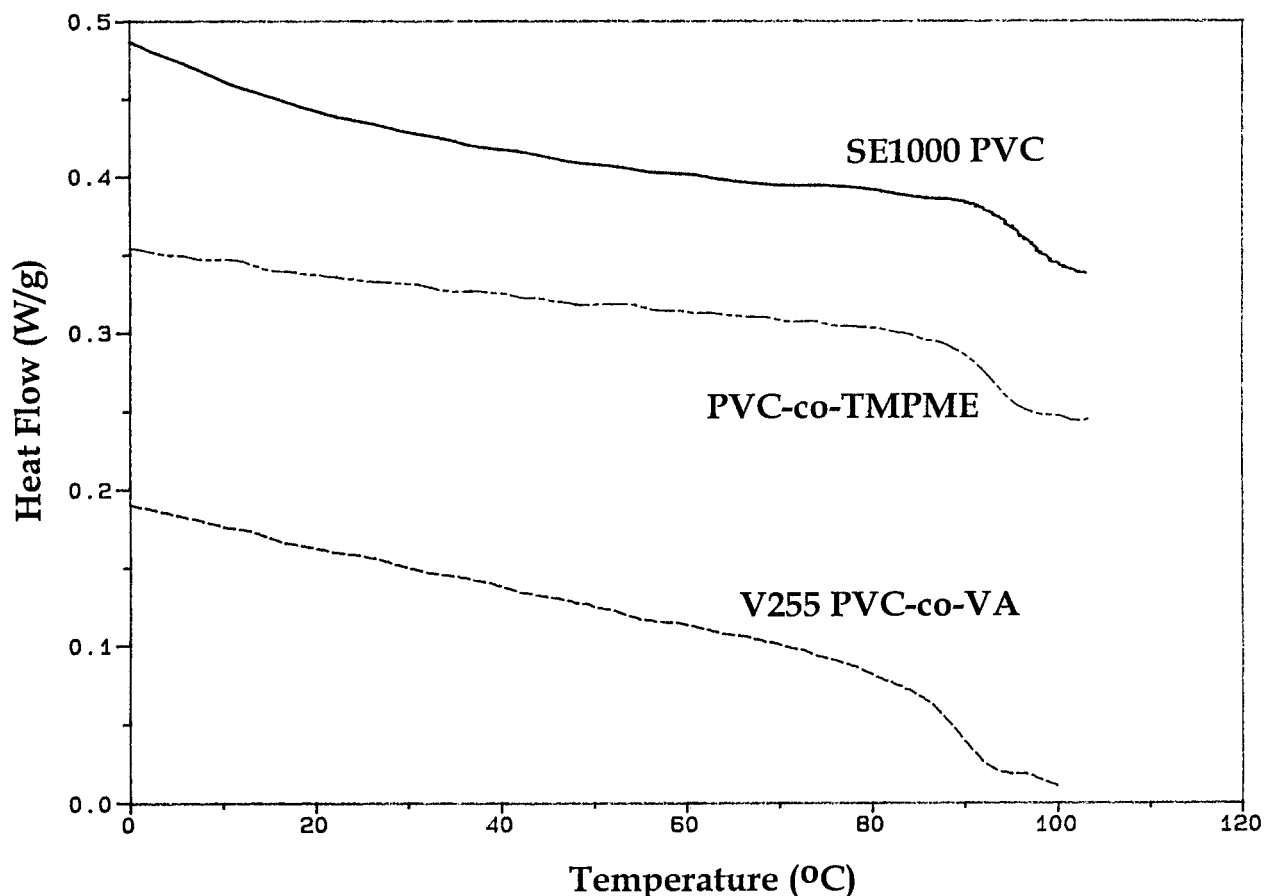
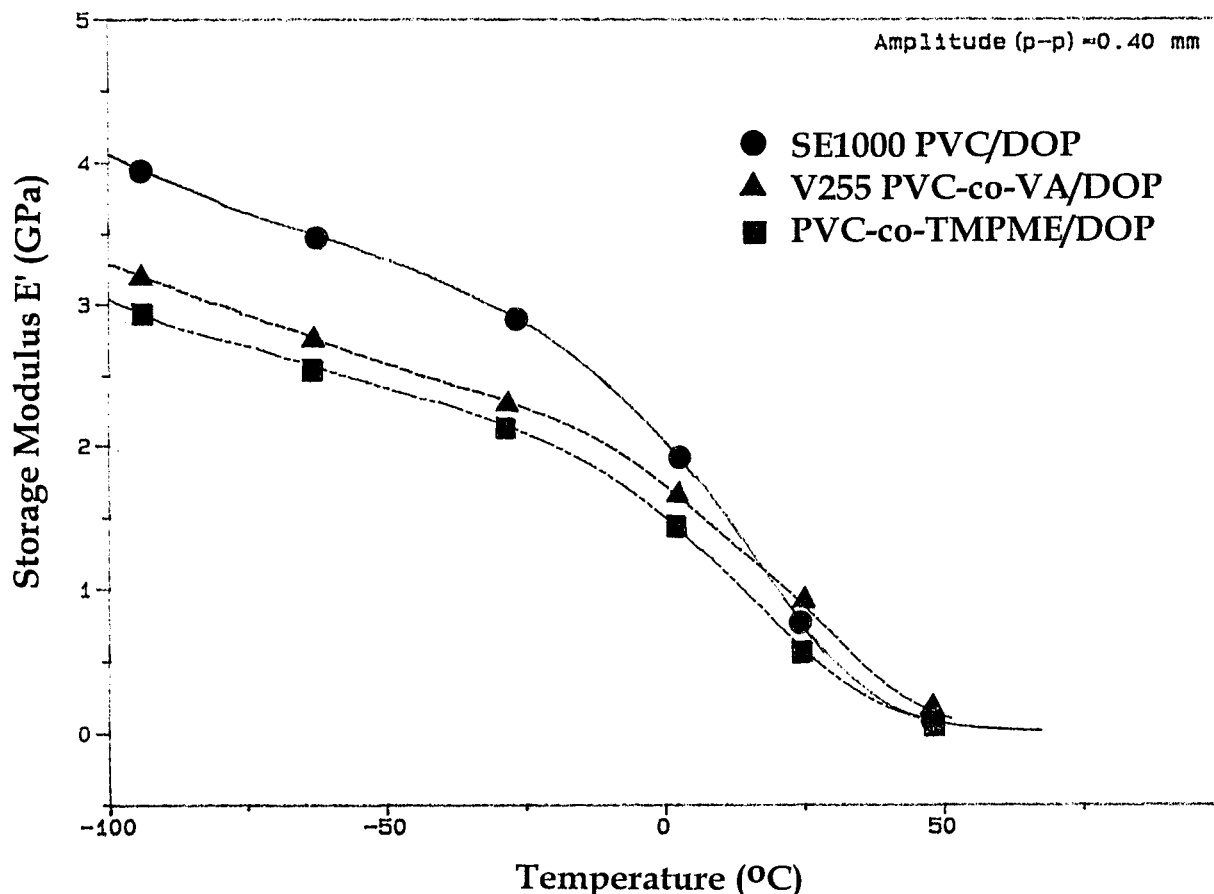**Figure 3**   DSC traces for PVC homopolymer, PVC-*co*-VA, and PVC-*co*-TMPME.

gents drawn at the inflections and are provided in Table II. These data show that small levels of comonomer may have a slight effect on T_g, but all three T_gs are close to that of the homopolymer resin. On the other hand, the thermal mechanical characteristics of the DOP plasticized copolymers (over the temperature range of −100 through 50°) are dramatically different from that of the plasticized homopolymer (as illustrated by the storage and loss modulae plots in Figs. 4 and 5). Figure 4 shows that the glassy state modulae (E') of the

Table II   Glass Transitions for Neat Resins, Taken from Second Run of Each Sample, Standard Error ± 3°C

Sample	Comonomer by Weight (%)	T_g (°C)
SE1000 PVC	0	93
V255 PVC-*co*-VA	5	85
PVC-*co*-TMPME	1.9	89

VA and TMPME copolymers are lower than the glass state modulus of PVC homopolymer. In addition, the plasticized homopolymer exhibits a glassy state loss modulus transition near −45°C (E'' in Fig. 5), which is not present in either of the copolymers. These data show that while both copolymers are similarly affected by DOP plasticizer, the PVC homopolymer is less efficiently plasticized by DOP.

It is well known that glassy state mechanical transitions in plasticized polymers can arise from either the motion of plasticizer, or from the motion of the main chain polymer itself.[15,16] Main-chain glassy state motion will result in better glassy state properties such as improved impact resistance, lower modulus, and a lower brittle−ductile transition temperature. On the other hand, plasticizer molecular motion without additional main chain motion has no positive effect on glassy state properties. In many cases, plasticizer motion in the glassy state is a consequence of plasticizer phase separation in the polymer matrix, which
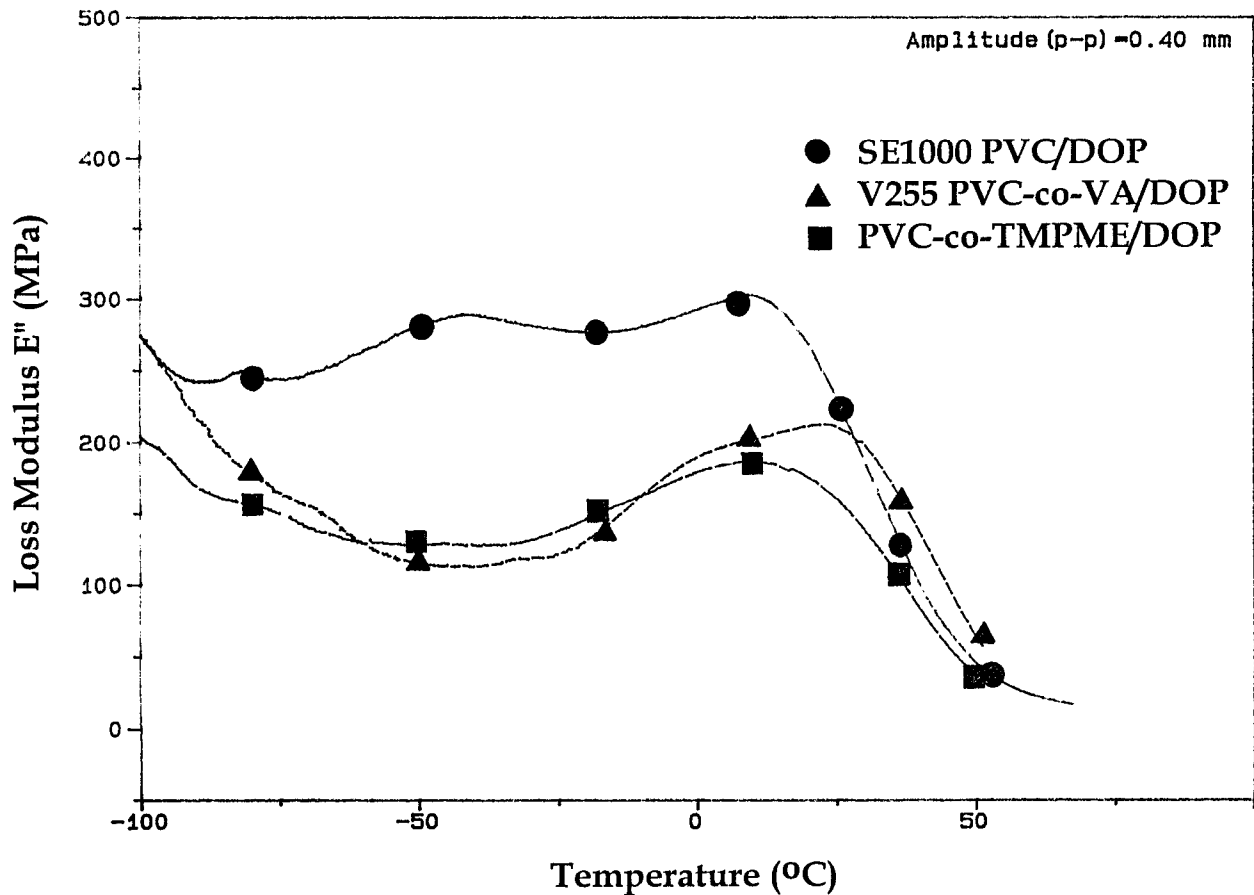
Figure 4 DMA storage modulae (E') versus temperature at 1 Hz for DOP plasticized PVC, PVC-*co*-VA, and PVC-*co*-TMPME.

has been found to be a function of plasticizer molecular structure, and hence, solubility in the polymer matrix.[16,17] In the case of plasticized PVC, microdomains of high plasticizer concentration can form to varying degrees depending on temperature and on the plasticizer structure. The migration of plasticizer into plasticizer rich domains can result in the formation of "rigid" domains with low plasticizer concentration, which in turn, can lead to a higher glassy state modulus.[18] The mechanical data in this study indicate that the morphology of the DOP plasticized homopolymer differs from that of the plasticized copolymers (as evidenced by the homopolymer's higher glassy state modulus, and by its low temperature loss transition). Thus, only a small level of VA (5%) or TMPME (1.9%) can have a significant effect on plasticizer compatibility.

Although the plasticized VA and TMPME copolymers exhibit similar thermal mechanical behavior to one another (through both the glassy and transition states ranging from −100 through 50°C), the copolymers exhibit different mechanical properties from one another at higher temperatures, as shown by the creep compliance data in Figure 6. The creep compliance curves illustrate the transition between the rubbery plateau and the point of chain disentanglement. This transition is known to depend on molecular weight, plasticizer type, plasticizer level, comonomer type, and comonomer level.[19] The data in Figure 6 show that homopolymer undergoes its transition at longer times than both of the copolymers. Given that the molecular weights of the three polymers are similar, it is likely that the shorter disentanglement transition times for the copolymers are a result of the presence of comonomer, and/or a difference in plasticizer compatibility. The VA copolymer has the shortest disentanglement transition time, probably because it has the highest comonomer level (5% VA vs. 1.9% TMPME). These data indicate that both the VA and TMPME copolymers have lower distortion temperatures than PVC homopolymer, and hence, should ex-

Figure 5 DMA loss modulae (E'') versus temperature at 1 Hz for DOP plasticized
PVC, PVC-*co*-VA, and PVC-*co*-TMPME.

hibit lower process temperatures than equivalently plasticized PVC homopolymer. The manifestation of this effect will likely depend on the level of comonomer that has been incorporated into the polymer chain. In this case, the maximum level of TMPME may be limited by a tendency for TMPME to inhibit the polymerization when used at higher levels.

Effect of Comonomers on Thermal Stability

Table III provides the time to blackening from static oven stability tests for the three plasticized polymers. These data show that the thermal stability of the TMPME copolymer is significantly better than PVC-*co*-VA, and slightly better than PVC homopolymer. The improved thermal stability is most likely related to the secondary stabilization effect of the trimethylolpropane functionality, which has been observed to improve thermal stability in the presence of Ba/Zn stabilizers, pos-

sibly through chelation of $ZnCl_2$ by the trimethylolpropane moiety.[9,12] This chelation would explain both the delay in the onset of degradation, and the improved stability when compared to homopolymer.

CONCLUSIONS

This study shows that TMPME can be copolymerized with VC monomer in a suspension polymerization process, and that the resultant polymer has better thermal stability than both PVC homopolymer and PVC-*co*-VA polymer. Both PVC-*co*-TMPME and PVC-*co*-VA are more efficiently plasticized by DOP than PVC homopolymer, as shown by a comparison of thermal mechanical characteristics in both the glassy and transition regions. The plasticized copolymers also exhibit lower distortion temperatures than plasticized PVC homopolymer as shown by creep compliance compari-
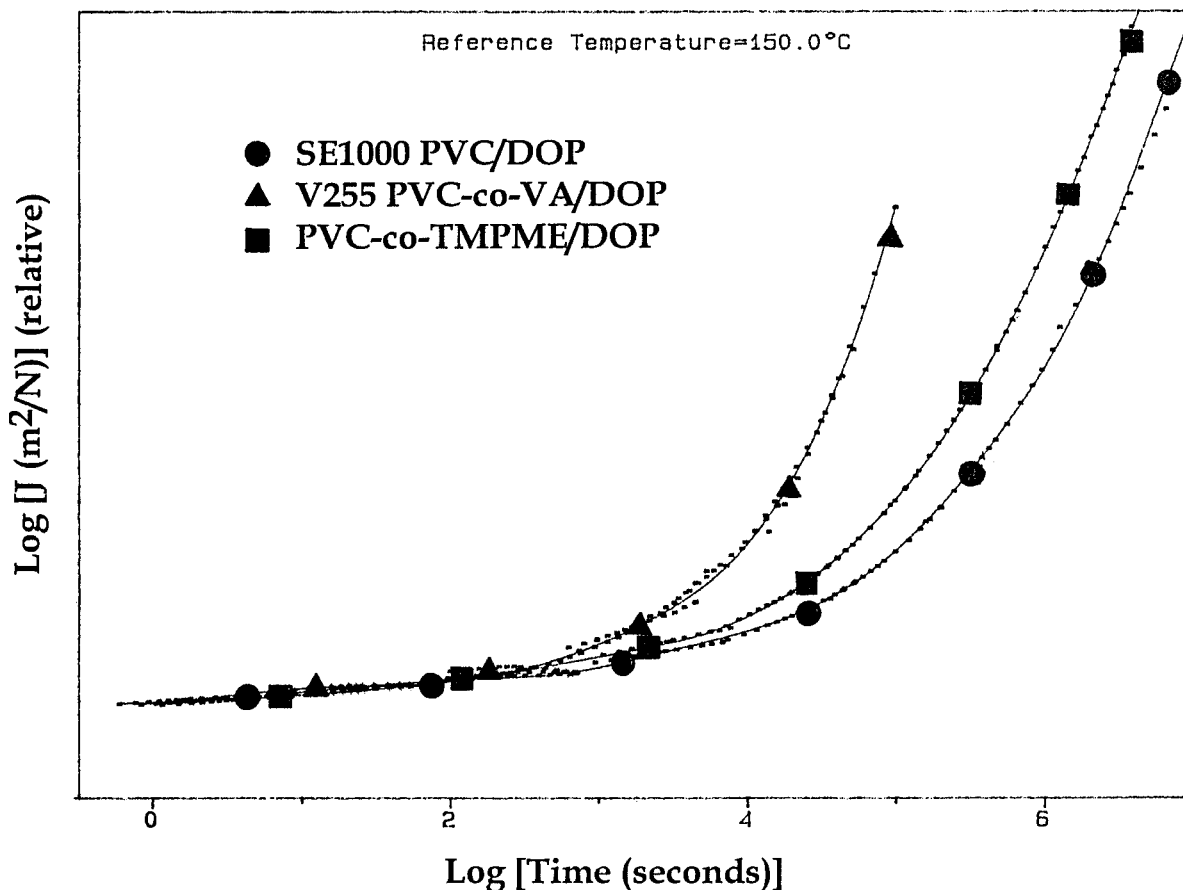
Figure 6 DMA relative creep compliance versus time from time–temperature–superposition master curves at a reference temperature of 150°C for DOP plasticized PVC, PVC-*co*-VA, and PVC-*co*-TMPME.

sons. In conclusion, it appears that PVC-*co*-TMPME can provide many of the conventional properties of PVC-*co*-VA without the detrimental effect of poor thermal stability. Thus, PVC-*co*-TMPME could be an improved substitute for PVC-*co*-VA in applications where the properties of PVC-*co*-VA polymers are desirable.

Table III   Time Interval to Decomposition as Evidenced by Blackening at 170°C and at 180°C from Static Oven Stability Tests of DOP Plasticized PVC, PVC-*co*-VA, and PVC-*co*-TMPME

Sample	Temperature (°C)	Time Interval to Decomposition (min)
SE1000 PVC	170	160–180
	180	80–90
V255 PVC-*co*-VA	170	40–60
	180	30–40
PVC-*co*-TMPME	170	180–200
	180	90–100

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