Star-Shaped Condensation Polymers: Synthesis, Characterization, and Blend Properties

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SYNOPSIS

A series of ϵ-caprolactone linear and star polymers were prepared and characterized in order to determine the effect of the star architecture (i.e., star number and arm length) on the morphology of these semicrystalline polymers. A spherulitic morphology was found in all the polymers investigated. However, for six arm stars containing low degrees of polymerization, it appears that the star core dominates its morphological behavior (presumably due to its relatively high volume fraction). The star core effects, however, are markedly reduced in star polymers where the arms contain higher degrees of polymerization.

The impact of the star core was further explored by investigating several poly(ϵ-caprolactone) (PCL):styrene–acrylontrile copolymers (SAN) blends. In all instances, miscible blends were the result because a single compositionally dependent glass-transition temperature (T_g) was observed. A moderate elevation in the T_g of the star-shaped polymers does occur, however, compared to their linear analogs. This effect is presumably due to the inability of the SAN chains to completely mix with all segments of star structure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Star-shaped macromolecules, whose arms are composed of essentially equal chain lengths, have been readily prepared by anionic polymerization methods. Because of their well-defined structure, a large amount of data has been compiled regarding their morphology, viscoelastic properties, and solution and melt behavior.[1–14] In these instances, star-shaped macromolecules are composed of essentially identical polymer chains, that is, arms of equal molecular weight radiating from a single and common junction point. The number of arms can also be readily controlled, thus making these polymers excellent model systems to determine the effects of macromolecular star architecture. For example, such polymers have proven quite useful in clarifying the rheological structure–property relationships of linear and star-branched polyisoprenes in shear and elongational flows.[15]

It is noteworthy that at identical molecular weight, the viscosity of a branched polymer is usually lower than its linear analog (at relatively low molecular weight). The viscosity of the former, however, increases at a more rapid rate with increasing molecular weight and exceeds the linear polymers at a specific molecular weight. This unique feature can be related to the result of restricted chain mobility due to branching. In addition, the local average polymer density is increased relative to that observed in a linear chain. Recent scattering measurements have shown that the swelling of star-branched polymers is consistent with a model of an inpenetrable core from which the arms of the star diffuse outward.[10] This shape exclusion (due to multiple chain branching) influences polymer–polymer blend miscibility as well as its corresponding phase diagram.[16] In fact, by substituting a star-branched polymer in place of a linear material of the same chemical constitution and molecular weight, useful information pertaining to core exclusion effects has been obtained.

In this study, the synthesis and characterization of a series of star-shaped condensation-typed polymers, that is, poly(ϵ-caprolactone) (PCL) are de-

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scribed. Both linear and star-shaped PCL were pre-
pared through the ring opening polymerization of
the lactone using various hydroxyl-containing com-
pounds as initiators. These polymers were investi-
gated by wide-angle x-ray scattering (WAXS), po-
larized light microscopy, and small-angle light scat-
tering (SALS) to evaluate the effect of branching
on the morphology of a semicrystalline polymer.

EXPERIMENTAL

Materials

ϵ-Caprolactone (99%), n-butyl alcohol (reagent),
ethylene glycol, pentaerythritol, and dipentaery-
thritol (tech.) were used as received (Alrich Chem-
ical Company). Stannous octoate (tech.) was ob-
tained from Pflatz and Bauer and used as received.

Polymerization

A typical polymerization procedure is as described.
Into a 150-mL, two-necked flask equipped with a
magnetic stirrer, condenser, and argon bubbler, ap-
proximately 50 g (0.43 mol) of ϵ-caprolactone was
added. The appropriate amount of hydroxy initiator
was then added with 50–75 mL of N,N-dimethyl
formamide (DMF). The mixture was heated to
150°C and, upon homogeneity, 0.05 g (1×10^{-4} mol)
stannous octoate was added as catalyst.

All reactions were maintained at the specified re-
action temperature for approximately 12 h to assure
total conversion of ϵ-caprolactone. The polymers
were isolated by precipitation into diethyl ether fol-
lowed by several washings with copious amounts of
the precipitating solvent. All samples were dried in
vacuum at 110°C for several days to remove any
trace amounts of DMF.

Characterization

NMR

Reactions were monitored using an IBM IR/32
FTIR Spectrometer. The small doublet at approx-
imately 860 cm^{-1} (found to be associated with the
cyclic, but not linear, ϵ-caprolactone ester) was fol-
lowed over time. The disappearance of this doublet
indicated 100% conversion of ϵ-caprolactone to lin-
ear polyester. ^{1}H NMR also confirmed that fact.

Polymer structures were confirmed by ^{1}H and ^{13}C
NMR on a Varian EX-300 using CDCl$_3$ as solvent
and tetramethylsilane (TMS) as internal reference.
^{1}H NMR was specifically used to determine star

**Table I Composition of Linear and Star
Poly(ϵ-Caprolactones)**

Designation	Number of Arms	Degree of Polymerization/Arm
1–9	1	9
1–22	1	22
1–30	1	30
2–12	2	12
2–20	2	20
2–30	2	30
4–12	4	12
4–20	4	20
4–26	4	26
6–10	6	10
6–18	6	18
6–37	6	37

structure, that is, the average degree of polymeriza-
tion ($\bar{\text{D}}$P) or chain length of each arm. The 3–5 ppm
spectral region contained the necessary resonances
for interpretation. The results of this analysis are
shown in Table I.
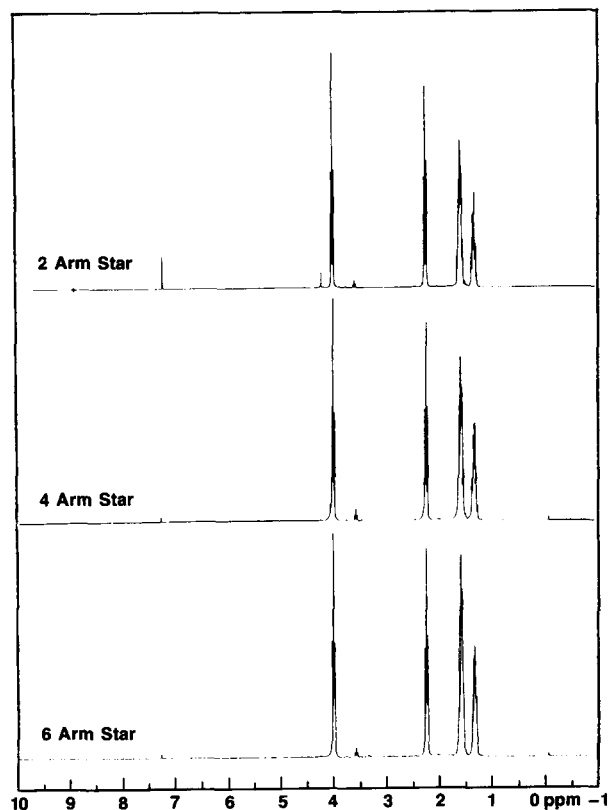
Polarized Light Microscopy

Thin films of each polymer were melt pressed be-
tween glass slides and examined under crossed polars
in a Nikon microscope. The morphological features
were recorded on Polaroid film type 667 under 400$\times$
magnification. (Typical exposure time was 0.5 s).

SALS

Light scattering measurements were obtained using
an SALS apparatus similar to that described by
Stein and Rhodes.[17] In brief, the instrument consists
of a Specta Physics Model 155 He–Ne gas laser op-
erating at a wavelength of 6350 Å, a rotatable po-
larizer on a Gaertner rotary film holder, a fixed an-
alyzer, and a photographic film holder. The exposure
times were regulated by a camera-type shutter.
Typical exposure times were 0.5 s using Polaroid
film type 55. Thin films (as previously described)
were analyzed as the spherulitic size was obtained
from the intensity maximum at an azimuthal angle
of 45° in the Hv scattering pattern.

Wide Angle X-Ray Scattering

The polyester powders were first molded (through
compression molding) into approximately 2 $\times$ 2
$\times$ 0.002 in. pads using the following conditions: 1-

−50°C. The thermal behavior was recorded during a second heating with the midpoint of the heat capacity change being defined as the glass-transition temperature, T_g.

RESULTS AND DISCUSSION

Linear and star polyesters of ε-caprolactone were prepared by the ring opening polymerization of the lactone. Various hydroxyl containing initiators were employed and stannous octoate was used as the catalyst. The final polymers were comprised of linear, two-arm, four-arm, and six-arm structures and were soluble in chloroform and DMF. The average chain length per arm varied approximately between 10 and 30 monomer units (Table I). The ¹H NMR of selected polymers are shown in Figure 1 and are all consistent with the structures depicted in Scheme 1.

Figure 1 NMR characterization of multi-arm poly(ε-caprolactone): two arm, $\overline{DP}/arm$ = 30; four arm, $\overline{DP}/arm$ = 20; six arm, $\overline{DP}/arm$ = 38.

min preheat at 212°F, followed by a 1-min press cycle at 29 tons at 212°F, followed by a 2-min cooling to room temperature under 29 tons pressure.

X-ray diffractometer scans were obtained using Cu Kα radiation in order to observe any changes in the PCL crystal structure. The angular range scanned was between 4 and 80°. The step size was 0.02° with sample time typically 50.0 s/degree. All measurements were obtained on the preformed melt processed pads having virtually identical thickness. The scattering times also remained invariant.
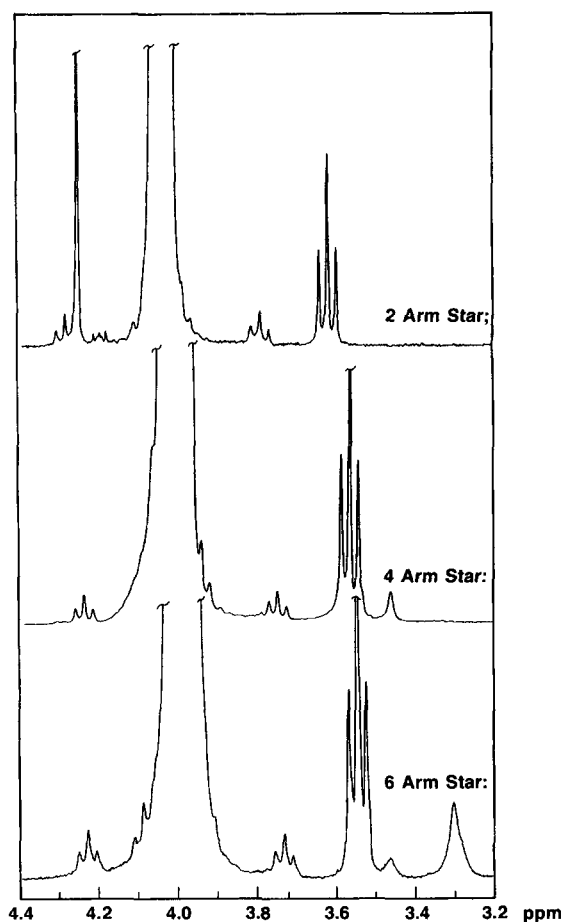
Thermal Measurements

Thermal analysis of the blends of poly(ε-caprolactone) and styrene–acrylonitrile (SAN) copolymer (20 wt % acrylonitrile) was performed in a Perkin–Elmer DSC-2 at a heating rate of 20°C/min. All DSC samples were weighed on a Perkin–Elmer AD-2 autobalance. Sample weight varied but typically ranged from 18 to 23 mg.

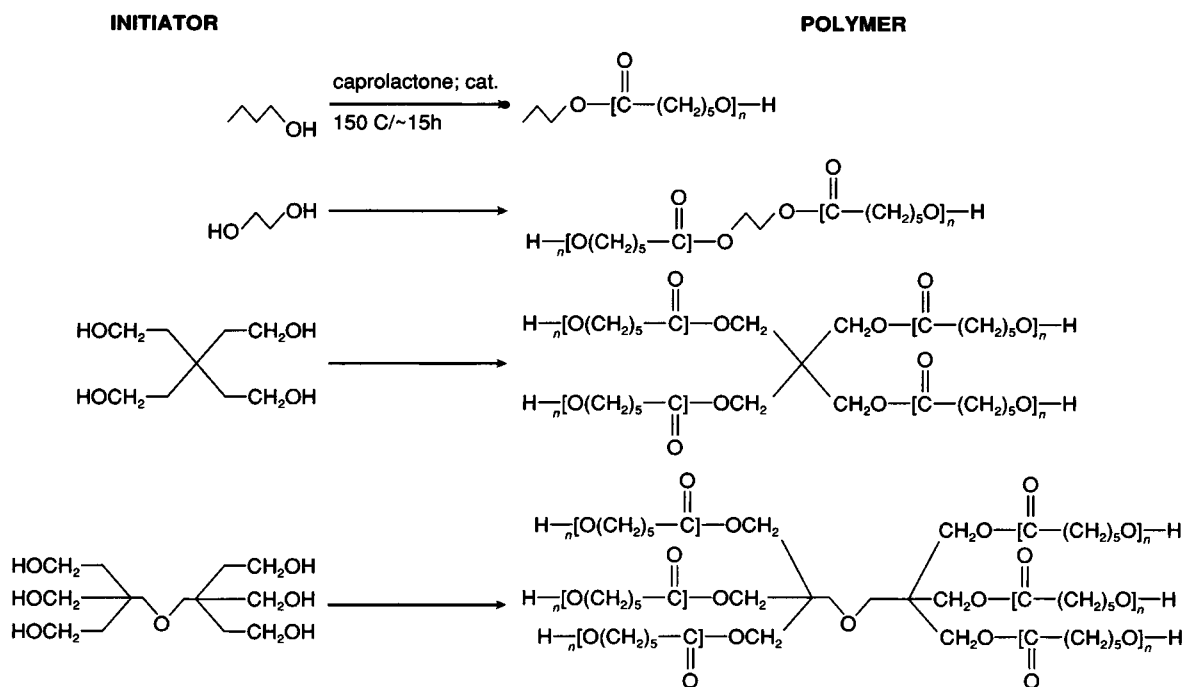Each sample was initially heated from room temperature to 190°C and then rapidly quenched to

Figure 2 NMR characterization of multi-arm poly(ε-caprolactone): two arm, $\overline{DP}/arm$ = 30; four arm, $\overline{DP}/arm$ = 20; six arm, $\overline{DP}/arm$ = 38.

INITIATOR   **POLYMER**

Scheme 1

The $\overline{DP}$ of each arm was also determined by ^1H NMR. The spectral region of 3–5 ppm contained the necessary resonances for the interpretation. The triplets and approximately 4.0 and 2.2 ppm are associated with the methylene units on the oxygen and carbonyl side (respectively) of the polyester. The smaller triplet at approximately 3.6 ppm corresponds to the terminal methylene protons adjacent to the hydroxy end group.

As shown in Figure 2, the amplified ^1H NMR spectra of 2, 4, and 6 arm star polymers show the two triplets at approximately 4.0 and 3.6 ppm corresponding to the oxygen bonded methylene adjacent to the polyester and terminal hydroxyl, re-

|← 4.0° →|

A   **B**
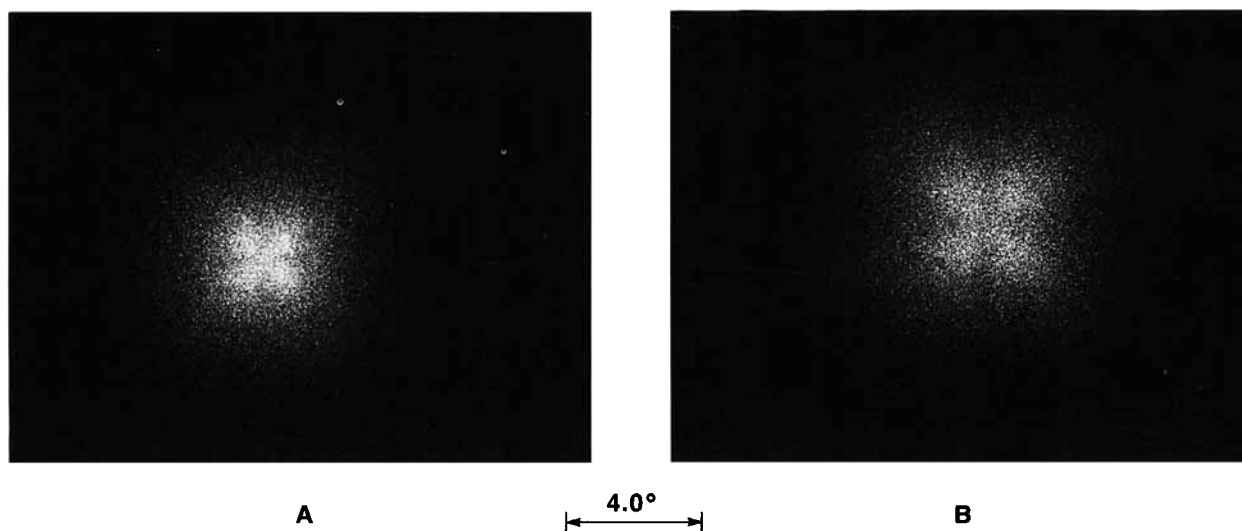
Figure 3   SALS scattering patterns (Hv mode) from linear poly(ε-caprolactone). (A) 2–12 and (B) 2–30.

A |◄──── **4.0°** ────►| B
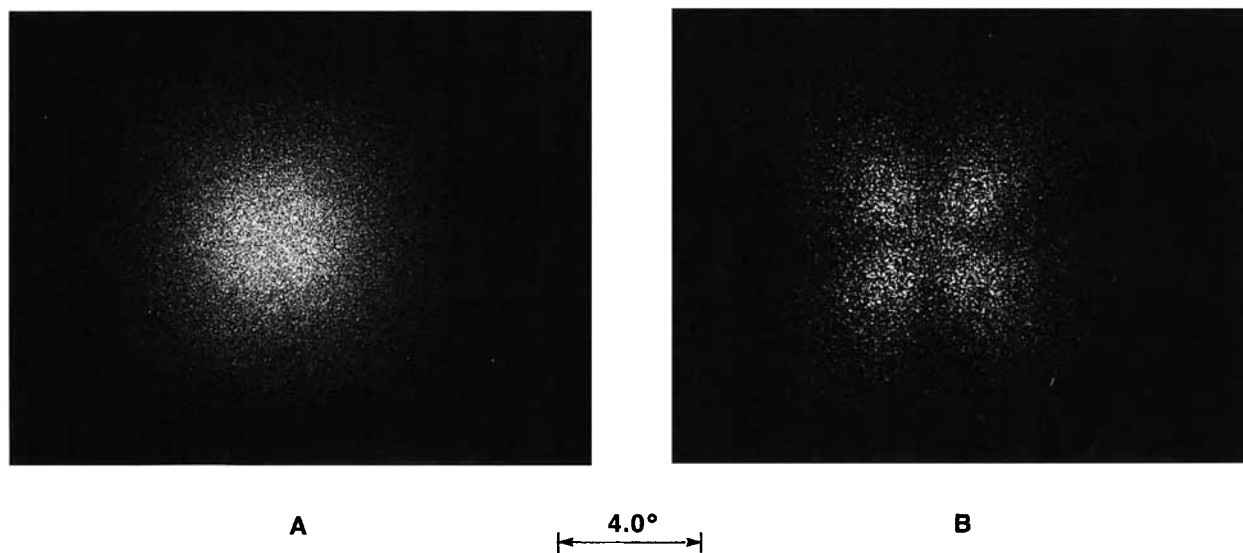
Figure 4   SALS scattering patterns from six-arm poly(ε-caprolactone). (A) 6–10 and (B) 6–37.

spectively. The average degree of polymerization was determined from the relative integration of these two triplets. In some cases, the star branch contributes its own resonance in this spectral region but nevertheless does not prevent the calculation of $\overline{DP}$.

SALS patterns were obtained on linear (Fig. 3) and star (Fig. 4) PCL. Only Hv scattering is reported here since these patterns are useful in distinguishing whether a spherulitic-type morphology is present.[17] Figure 3 shows typical scattering patterns from linear PCL as a function of molecular weight. In all the linear polymers synthesized for this study, a spherulitic morphology is observed as noted by the

four-leaf clover pattern with its corresponding maximum in intensity of an azimuthal angle of 45°. This structure is observed in our polarized microscopy examination of these polymers. The distinguishing feature of this data is the moderate decrease in spherulitic radius with increasing molecular weight. Because all samples were prepared under the identical thermal condition, the size change can be related to the melt viscosity.

On the contrary, a spherulitic morphology was not found in the six-armed star PCL polymer containing the lowest arm degree of polymerization. Apparently, the behavior of these short arms tethered to a core do not possess sufficient mobility for


A |◄── **10 μm** ──►| B
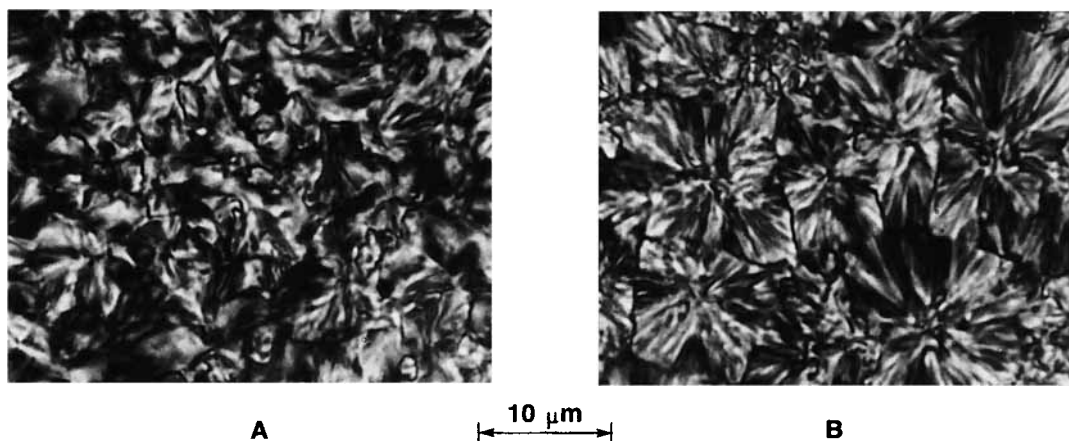
Figure 5   Polarized light micrographs from six-arm poly(ε-caprolactone). Magnification is 400×. (A) 6–10 and (B) and 6–37.

this to occur. However, a spherulitic morphology is observed when the arm molecular weight is increased. The SALS and polarized light micrographs of these six-armed stars is presented in Figures 4 and 5, respectively. As noted previously, the salient feature in the Hv scattering for the longer arm polymer is the intensity maximum at an azimuthal angle of 45° in the clover leaf pattern. The scattering pattern found in the short arm PCL star can be described as corresponding to crystallites dispersed and randomly oriented in the amorphous matrix.[18,19] It appears that under these conditions of film formation, that is, rapid cooling from the melt, the short tethered chains do not possess the necessary chain flexibility to form a spherulitic superstructure even though the linear analog can form this structure. Graessley[20] pointed out that the equilibrium time for the conformational fluctuations of a tethered chain would be four times longer than for a untethered linear chain. Recent dielectric spectroscopy investigation on the molecular dynamics in linear and star-shaped polymers confirms this prediction. The branch point within a star-shaped chain strongly inhibits simple reptational motion and as a result, relaxation of the chain occurs by a much slower process of contour length fluctuations. Although these measurements were made on noncrystalline polymers, the change in the chain dynamics should have a marked influence on the properties of tethered chains that can crystallize.

We conclude from these observations that as the core becomes a substantial fraction of the star volume, the behavior, that is, structure–physical properties, will be altered. It is, however, noteworthy that four-arm PCL stars from a spherulitic morphology spanning essentially the same molecular weight range. Apparently, segmental core density and molecular weight can markedly influence behavior. This occurs even though the basic crystal structure remains invariant to the above structural modifications as observed in the wide-angle x-ray scattering data on both linear and multi-arm PCL stars (Fig. 6).

It is of general interest to examine the phase behavior of linear and star-shaped polymers in a blend system. PCL is of particular interest due to its miscibility with a relatively large number of polymers including SANS.[21-24] These latter copolymers are miscible if the acrylonitrile content is between 8 and 28 wt %. A preliminary examination of the influence of a linear and star-shaped polymer is shown in Figure 7. The data confirms that the T_g of the latter blends are consistently higher than their linear counterparts. The six-arm star chosen for these
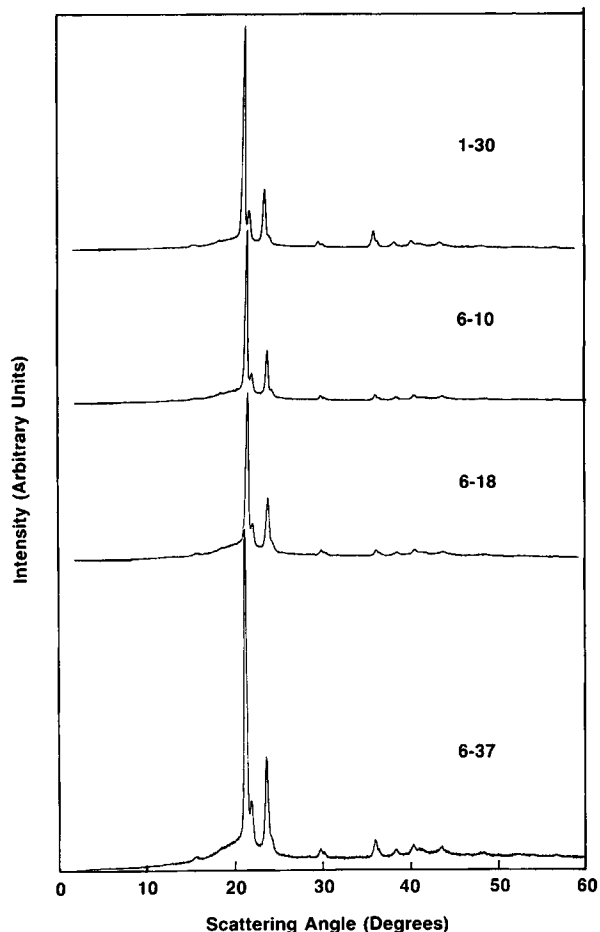

Figure 6 Wide-angle x-ray scattering profiles from linear and a series of six-arm poly(ϵ-caprolactone) containing varying arm degrees of polymerization.

thermal measurements has the lowest molecular weight arms and therefore the highest fraction of its volume as core material. As a result, it appears that only a fraction of the PCL chain is miscible with SAN resulting in a moderate elevation in T_g. Presently, it appears that normal thermal behavior is observed for all of the four-arm star-shaped polymers. It is noteworthy that at high PCL contents, crystallinity impaired our ability to determine the unperturbed T_g of the blends.

CONCLUSION

A series of linear and star-shaped poly(ϵ-caprolactone) materials were synthesized and characterized. It has been demonstrated that the morphology of these materials behave in a similar manner except for a six-arm star having low arm molecular weight.
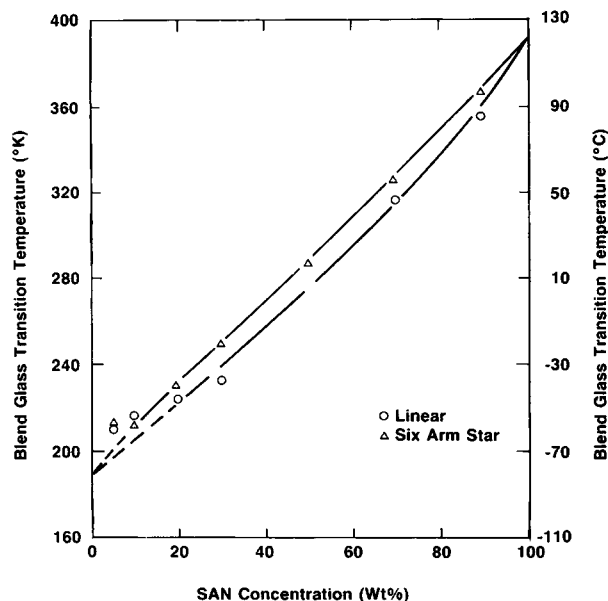
Figure 7 Thermal behavior of a blend of SAN and (○) a linear (1-9) and (△) a six-arm poly(ε-caprolactone) (6-10).

In this particular case, the expected spherulitic morphology (as determined by SALS and polarized light microscopy) is markedly deteriorated to a structure that is best described as a random arrangement of lamellae dispersed in an amorphous matrix. This can be attributed to the apparent high volume fraction and high segment density of the chains within the core of star polymers. The restrictions imposed on these segments also influence blend properties. Even though miscible blends can be produced by mixing both linear and star-shaped PCL with SAN, it appears that the SAN chains are unable to penetrate in an efficient manner into the core region resulting in elevated glass-transition temperatures.

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