

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Lactone Polymerization and Polymer Properties

G. L. Brode^a; J. V. Koleske^b

^a Research and Development Department, Chemicals and Plastics Union Carbide Corporation, Bound Brook, New Jersey ^b Research and Development Department, Chemicals and Plastics Union Carbide Corporation, South Charleston, West Virginia

To cite this Article Brode, G. L. and Koleske, J. V.(1972) 'Lactone Polymerization and Polymer Properties', Journal of Macromolecular Science, Part A, 6: 6, 1109 – 1144

To link to this Article: DOI: 10.1080/10601327208056888

URL: <http://dx.doi.org/10.1080/10601327208056888>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Lactone Polymerization and Polymer Properties

G. L. BRODE

Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
Bound Brook, New Jersey 08805

and

J. V. KOLESKE

Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia 25303

ABSTRACT

The polymerization of lactones provides a facile route to polyesters that is unimpeded by the long reaction cycles and elevated temperatures inherent in the condensation of hydroxyl and acid functional groups. Depending on the structure of the lactone monomer, catalyst/initiator systems are known which allow preparation of extremely high molecular weight polyesters of low polydispersity. In addition to obtaining high molecular weight polyesters in relatively short reaction cycles and at moderate temperature, lactone polymerization allows careful control of polymer end groups through proper selection of the initiating species. The type of end group plays an important role in both the thermal stability and hydrolytic stability of the resulting polyester. This study reviews and updates the field of lactone polymerization with specific emphasis on the chemistry and rheological

properties of polyesters derived from ϵ -caprolactone and related monomers. Consideration will be given to the effect of polymer end groups on polycaprolactone stability, to the modes by which polyesters may decompose, and to the factors influencing the possibility of monomer insertion into the metal hetero-atom bond of various catalyst systems. Poly- ϵ -caprolactone appears unique in its ability to blend with a variety of both amorphous and crystalline polymers over wide composition ranges. Studies show that three types of blends can be obtained with poly- ϵ -caprolactone, wherein the polymer mixtures appear to be crystalline interaction products, truly compatible blends, or mechanically compatible blends. The physical and mechanical properties of selected blends are presented and discussed.

INTRODUCTION

The polymerization of many lactone monomers represents a facile route to the corresponding polylactone or polyester. Problems associated with condensation polymerization include by-product removal; the necessity for exact stoichiometry, especially with high molecular weight diols; high temperatures and long reaction cycles to obtain even moderate molecular weight products; side reactions such as etherification and dehydration to olefin; and end group control. In contrast, lactone polymerization, which proceeds by a ring-opening process, can lead to extremely high molecular weight polyester in comparatively rapid cycles and at lower reaction temperatures. Furthermore, depending on the catalyst/initiator system employed, such advantages can result while exact control of the terminal functions is maintained. This particular factor can be important in end-use applications for the polyester. The synthesis and polymerization of various lactone monomers has been recently reviewed [1] and will not be discussed in this article. Rather, some of the more recent observations in lactone chemistry will be presented. Major emphasis will be placed on ϵ -caprolactone and the physicochemical aspects of the resulting polymer, on the methods of polymerizing lactones, and on the factors which affect the stability of polylactones.

LACTONE POLYMERIZATION SYSTEMS

Lactones can generally be polymerized by one or more of the three types of systems listed in Table 1. Numerous examples of each

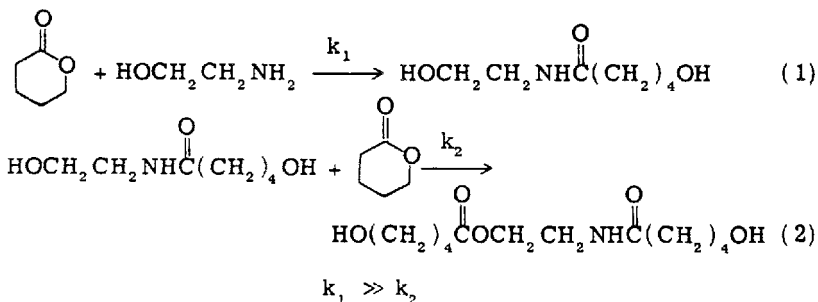
TABLE 1. Lactone Polymerization Systems

Type	System	Examples
1	Active hydrogen initiator, no catalyst	ROH, RNH ₂ , etc.
2	Nonactive hydrogen initiator, or catalyst only	R ₂ Zn, Sn(OR) _{2,4} , etc.
3	Active hydrogen initiator plus catalyst	ROH + Ti(OR) ₄ , etc.

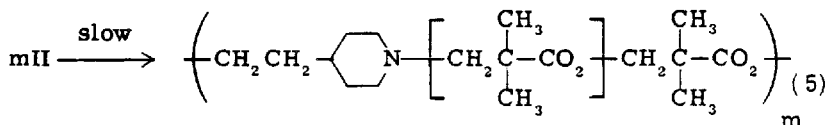
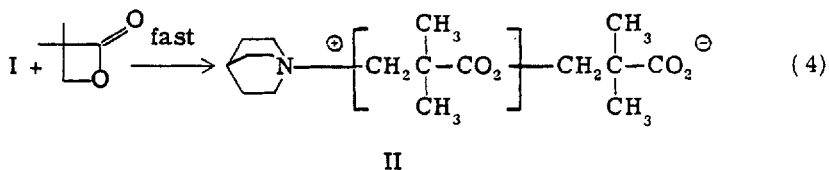
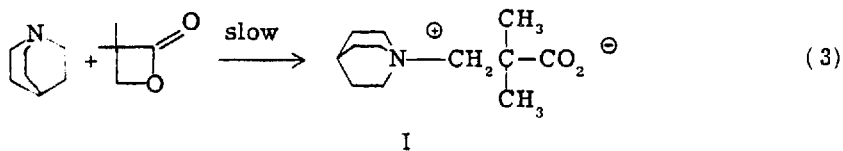
type have been reported, and the examples given in Table 1 are used only for illustrative purposes.

Uncatalyzed, Active Hydrogen-Initiated Polymerizations

Uncatalyzed lactone polymerization (Type 1, Table 1) with conventional active hydrogen initiators such as alcohols, amines, and carboxylic acids are relatively slow reactions and are restricted to the synthesis of low molecular weight polyesters. For example, the ethylene glycol-initiated polymerization of ϵ -caprolactone [2] requires a reaction cycle of 35 hr at 190°C for quantitative conversion and for molecular weights of about 5000. Kinetic studies on the polymerization of δ -valerolactone, initiated either with ethylene glycol or ethanolamine, at temperatures up to 200°C showed that although a rapid reaction occurs between monomer and the amino group, (Eq. 1), this reaction is followed by a slow propagation reaction involving addition of monomer to the end hydroxyl group of the polymer chain (Eq. 2).



An apparent exception to this rule that uncatalyzed lactone polymerizations are relatively slow is the uncatalyzed polymerization of pivalolactone to high molecular weight and high conversion by using strained cyclic amines as initiators [4]. In this rather unique polymerization scheme, a cyclic amine/pivalate betaine, I, is proposed as the initiating species (Eq. 4). Carboxylate attack on the cyclic ammonium ion is apparently a slow step and results in charge neutralization, with molecular weight build-up (Eq. 5). Betaine formation has been previously reported [5] from the reaction of tertiary amines with β -propiolactone and, therefore, this particular type of uncatalyzed polymerization, illustrated in Eq. (3)-(5), is probably restricted to highly strained lactone systems and would not be expected to be characteristic of lactones of larger ring size.



Nonactive Hydrogen-Initiated Polymerizations

High molecular weight polyesters can be prepared using anionic or cationic catalysts or initiators (Type 2, Table 1), as the case may be. Numerous examples of such systems have been described in the literature. While nonactive hydrogen initiators have, on occasion, been referred to as catalysts, a clear distinction should be made between the two materials. Strictly speaking, a catalyst does not enter into the reaction in the sense that an initiator does and should only influence reaction rate. In contrast a nonactive hydrogen

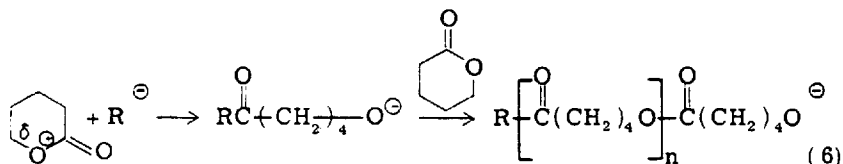
initiator, while it may also be a catalyst, does affect polymer molecular weight. One example of this latter system is the dibutyl-zinc-initiated polymerization of ϵ -caprolactone, wherein polymer molecular weight was found to be inversely proportional to dibutyl zinc concentration [6]. Organometallic catalysts such as stannous diacylate or stannic tetracylate have been used without active hydrogen initiators to obtain poly- ϵ -caprolactone of at least 100,000 molecular weight [7]. Dimethyl cadmium, methyl magnesium bromide, dibutyl zinc, etc., are also effective catalysts (initiators?) for preparing homopolymers and copolymers from δ -valerolactone, ϵ -caprolactone, and their respective alkyl substituted derivatives with average molecular weights as high as 250,000 [8] being obtained. Similarly, β -lactones have been polymerized to very high molecular weight polymers, without the use of active hydrogen initiators, using catalysts or initiators such as tertiary phosphines [9], butyllithium, naphthyl sodium, triethyl aluminum, and methyl zinc chloride [10]. The absence of active hydrogen initiators generally results in poor control of both molecular weight and polymer end groups. An exception to this generality may be in the use of dianions as in the preparation of styrene-pivalolactone block copolymers initiated with "living" polystyrene dianion [11].

Catalyzed, Active Hydrogen-Initiated Polymerizations

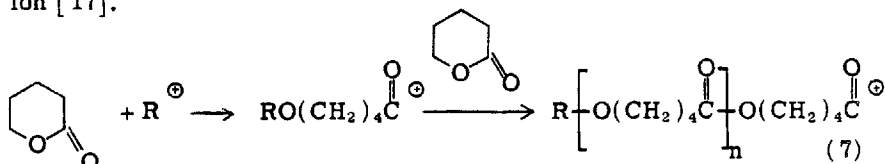
Molecular weight and end group control can be obtained by use of an active hydrogen initiator in conjunction with a catalyst (Type 3, Table 1). Polyols, polyamines, carboxylic acids, etc., have been used with catalyst systems such as zinc or lead salts [12], alkyl titanates [12], stannous esters [13], stannic esters [14], and phosphines [15] to control molecular weight and polymer end groups.

MECHANISM OF LACTONE POLYMERIZATION

Detailed studies on the mechanism of lactone polymerization are limited. However, studies by several workers suggest that anionic polymerization of lactones involves acyl-oxygen fission with propagation through an alkoxide anion [16] as described in Eq. (6).



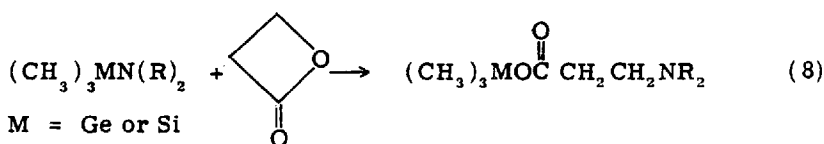
Cationic catalysis, on the other hand, in the absence of active hydrogen initiators, is suggested to involve propagation through a carbonium ion (Eq. 7), with acyl-oxygen cleavage being the prime mode of ring opening [16, 17]. Alkyl-oxygen fission does apparently take place in unique cases, such as with β,β -dimethyl- β -propiolactone, due to the increased stability of the resulting tertiary carbonium ion [17].



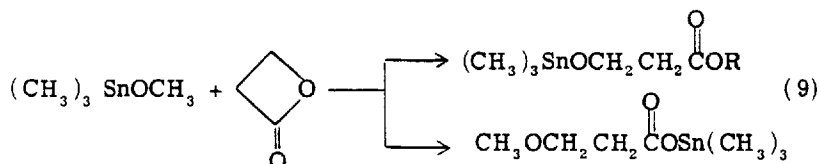
In the presence of an active hydrogen compound, where a carbonium ion intermediate would not be possible, cationic catalysts are postulated to aid in the acyl-oxygen fission process, although specific intermediate structures, e.g., carbonyl oxygen complexes vs ether oxygen complexes, have not been proposed [3, 17].

Insertion Reactions

Incorporation of catalyst residues, as polymer end groups, would be expected in many systems initiated with active hydrogen compounds. Of more fundamental importance, especially from the viewpoint of polymer stability, is the possibility of catalyst incorporation into the backbone of the polymer. Recent publications document the insertion reaction of lactone monomers into the metal hetero-atom of certain organometallic compounds and indicate that catalyst incorporation into the polymer backbone may indeed take place. For example, propiolactone has been reported to react with (trimethylgermyl or trimethylsilyl) dialkylamines to yield the corresponding insertion products through selective alkyloxygen cleavage [18] (Eq. 8).

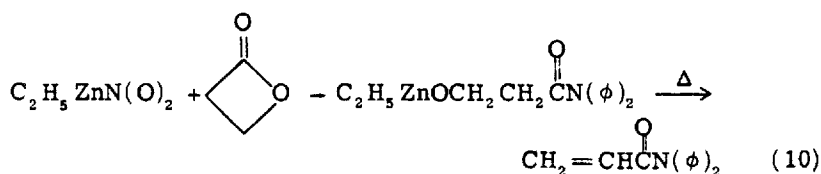


Trimethyltin methoxide, on the other hand, leads predominantly to acyl-oxygen fission, although the ratio of acyl-oxygen to alkyl-oxygen fission was found to be a function of the polarity of the medium, with solvents of low dielectric constant (carbon tetrachloride) producing exclusively the former [19, 20] product (Eq. 9).

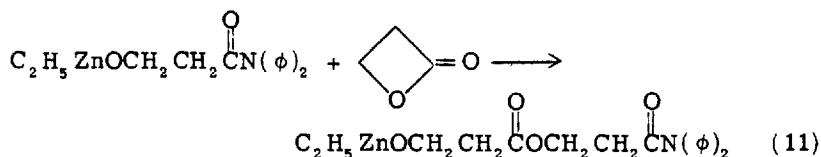


Similar insertion reactions have also been observed with propiolactone or other cyclic esters and zinc or aluminum compounds.

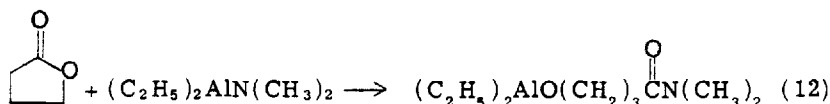
Acyl-oxygen cleavage appears to be the exclusive reaction that takes place with (ethylzinc) methoxide or (ethylzinc) diphenylamine [21]. It is interesting to note that the latter compound is reported to exhibit poor thermal stability (Eq. 10).



Furthermore, evidence was presented [21] for successive insertion of monomer units into the Zn-O bond. This suggests another mechanism by which lactone polymerization (and catalyst-initiator incorporation) can occur as shown in Eq. (11).

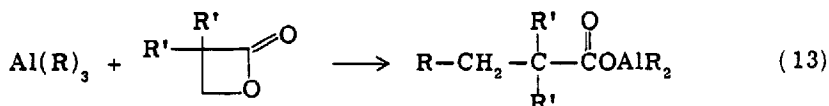


Aluminum compounds were also found to undergo insertion reactions. (Dimethyl aluminum) dimethylamine or ethoxide reacted with propiolactone, or five-membered ring lactones, exclusively by acyl-oxygen fission (Eq. 12) whereas (diethylaluminum) ethyl



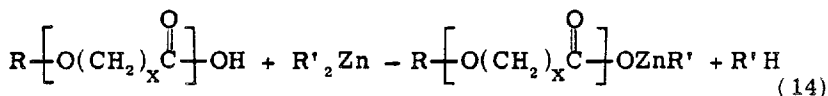
sulfide yielded acyl-oxygen or alkyl oxygen cleavage with propiolactone [22]. While the references cited to this point have involved

insertion into a metal hetero-atom, one reference was found involving insertion into a metal-alkyl bond. Trialkyl aluminum compounds were reported to react with α,α -disubstituted propiolactone to yield the corresponding aluminate ester in quantitative yield [23] (Eq. 13).



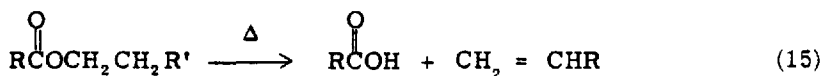
POLYMER STABILITY

Insertion into the polyester backbone with organometallic catalyzed or initiated lactone polymerizations can have serious ramifications with regard to polymer stability. Such linkages would be expected to convey both hydrolytic and thermal instability. As illustrated with propiolactone and (ethylzinc) diphenylamine in Eqs. (10) and (11), chain growth by repetitive insertion of the lactone into the tin hetero-atom bond would be one method for incorporation of a hydrolytically and thermally unstable linkage into the polymer backbone. Catalyst incorporation could also result from the reaction of an organometallic compound with an active hydrogen end group of a growing chain or initiator molecule (Eq. 14). The latter type of



incorporation would be even more deleterious in systems initiated with carboxylic acids as a result of the autocatalysis that would result in the hydrolysis of such a structure, i.e., regeneration of carboxylic acid groups. From work on hydrolysis of poly(ethylene terephthalate) [24, 25], the rate of hydrolysis is proportional to the acid content.

Based on extensive investigations of the pyrolytic decomposition of simple esters, β -elimination is a chief decomposition mechanism that occurs when a hydrogen atom occupies a position beta to the ether oxygen of the ester function [26-29] (Eq. 15).



Although polyesters appear to be somewhat more complex in their modes of decomposition, e.g., thermo-oxidation [30] vs nonoxidative [31-33] thermal decomposition, the classical cyclic mechanism also appears to be applicable. Decomposition by this mechanism takes place at temperatures well above 200°C, with random degradation of a number of aliphatic polyesters beginning at around 275°C [32]. Similar stability would be anticipated for many polyesters derived from lactone polymerization, provided catalyst insertion has not occurred, polymer terminal groups are of a stable variety, and the tendency for depolymerization to monomer is not excessive. Poly- ϵ -caprolactone, for example, reportedly does not begin to depolymerize to monomer up to temperatures in excess of 270°C [34], whereas poly- δ -valerolactone begins to depolymerize at temperatures of 180°C unless the hydroxyl end groups have been acetylated, in which case excellent stability is observed to at least 200°C. Low molecular weight, hydroxyl-terminated poly- ϵ -caprolactone was found to depolymerize to monomer, dilactone, trilactone, and minor amounts (~5%) of other products at 250 to 300°C when tetrabutyl titanate, metal chlorides, and various other catalysts were employed [35]. A significant aspect of this work was the high yield (~33%) of the macrocyclic, 14-membered dilactone of ϵ -caprolactone that was obtained when the titanate catalyst was used.

The catalyst (initiator), catalyst concentration, and type of end group have been found to be extremely important insofar as the thermal and/or hydrolytic stability of poly- ϵ -caprolactone is concerned. For example, poly- ϵ -caprolactone prepared with a dibutylzinc catalyst exhibits a rapid decrease in molecular weight when exposed to 120°C for short periods of time [36]. Copolymers of ϵ -caprolactone and ϵ -methyl- ϵ -caprolactone exhibited similar thermal instability and also displayed a gradual molecular weight decrease over long periods at ambient temperatures [6]. The reason(s) for molecular weight decrease with this catalyst system, e.g., catalyst insertion into the polymer backbone, type of end group, or polyester reequilibration, is not clear. However, certain evidence that may suggest insertion of the lactone molecule into the metal-alkyl bond in this system is described in the Dilute Solution Properties section.

Poly- ϵ -caprolactone or ϵ -caprolactone copolymers prepared with phosphorous pentafluoride also exhibit instability. Furthermore, certain tin catalysts, e.g., stannous octanoate, can result in thermal instability as shown by the data in Table 2. The effect of catalyst concentration is clearly seen in these data [36]. Carboxylic acid end group concentration was held constant in these experiments (*vide infra*).

The effect of stannous octanoate concentration on polymer molecular weight, as shown in Table 2 is noteworthy. Since

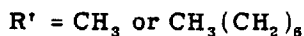
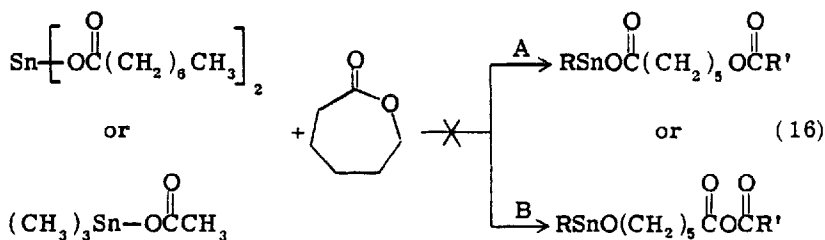
TABLE 2. Thermal Stability of Poly- ϵ -caprolactone/Stannous Octanoate Catalyst [36]

Sample No.	Stannous octanoate (ppm)	Thermal treatment ($^{\circ}\text{C}/1$ hr)	Reduced viscosity ^a		Melt flow ^b ratio
			Initial	Final	
1	400	220	0.84	0.74	1.9
2	400	250	0.84	0.58	5.2
3	2000	220	0.65	0.51	2.8
4	2000	250	0.65	0.43	7.7

^a Measured at 0.2 g/dl in benzene at 30 $^{\circ}\text{C}$.

^b Melt flow ratio = grams of polymer extruded at 100 $^{\circ}\text{C}$ (constant pressure) initially divided by grams of polymer extruded at 100 $^{\circ}\text{C}$ after exposure at T ($^{\circ}\text{C}$) for 1 hr.

initiator concentration was held constant, this and similar molecular weight data suggested that stannous octanoate was behaving as an initiator as well as a catalyst. Efforts to detect lactone insertion into stannous octanoate or trimethyl tin acetate (Eq. 16), using equivalent



concentrations of caprolactone per tin ester function under a variety of experimental conditions (solvents of various dielectric constant and neat reactions), failed to show any trace of such an insertion reaction either by alkyl-oxygen or acyl-oxygen cleavage. The conclusion that insertion does not occur with stannous octanoate or with trimethyltin acetate is based on IR, mass spectroscopy, and NMR analyses of the reaction mixtures [37]. Particularly in the case of trimethyltin acetate, even slight changes in molecular structure

would be expected to result in relatively large changes in the chemical shifts (at least several hundredths of a part per million) and multiplicities of the acetoxy and methyl resonances as has been demonstrated with related systems [38, 39]. In fact, no such changes were observed with the system. The data obtained indicate only the presence of unreacted tin ester, caprolactone monomer, and a small amount (20% or less) of poly- ϵ -caprolactone. The NMR spectral data are summarized in Table 3. Although it is not presented, the mass spectroscopic analysis also failed to show any fragmentation patterns indicative of an insertion reaction. It was anticipated that the products from acyl-oxygen fission, Path B, would be unlikely, since a relatively high-energy anhydride bond would be formed in such a process. However, the complete absence of insertion products by alkyl-oxygen cleavage, Path A, was somewhat surprising.

The deleterious effect of carboxylic acid end groups on the thermal stability of poly- ϵ -caprolactone is evident from the data in Table 4 [36]. Samples prepared with "high" acid numbers (polymers 2, 3, and 4, Table 4) display significantly reduced thermal stability. An acid number of 1.8, at a number-average molecular weight of 20,000, corresponds to ~ 0.65 carboxyl groups/molecule.

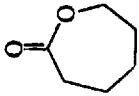
Carboxyl end groups also display a deleterious effect on polymer molecular weight at ambient temperatures over prolonged periods of time. This is shown by the data listed in Table 5. Once again, the effect is greatest at the higher acid numbers (cf. Sample 1 with Samples 3-5 in Table 4). Unfortunately, there was not sufficient data to conclusively establish the molecular weight decrease as an autocatalytic one. However, from other experiments the decrease was clearly related to a hydrolysis reaction.

Based on these various considerations and factors, a proprietary system was developed for the preparation of poly- ϵ -caprolactone and caprolactone copolymers. This system results in polymers with both excellent thermal stability and long-term ambient temperature stability as shown by the data in Tables 6 and 7. No attempt was made to exclude oxygen during the melt stability experiments, nor were antioxidants incorporated into the polymers.

PROPERTIES OF POLY- ϵ -CAPROLACTONE

Poly- ϵ -caprolactone is a partially crystalline polymer. Bittiger and co-workers [40] studied the crystal structure of the polymer and found that it has an extended planar zigzag chain conformation with the unit cell orthorhombic in character. It has a crystalline structure that bears a close similarity to that of polyethylene with the a and b dimensions of the two polymers being almost identical. Calculated polymer

TABLE 3. Chemical Shifts of Protons of Trimethyl Tin Acetate, ϵ -Caprolactone, and Polycaprolactone^a [37]

$(\text{CH}_3)_3\text{SnOAc}$	$(\text{CH}_3)_3\text{Sn}-$	$-\text{OCCCH}_3$	$-\text{OCCCH}_2$	$-(\text{CH}_2)_4$	$-\text{CH}_2\text{OC}-$
	9.46 Singlet	7.46 Singlet	-	-	-
	-	-	7.35 Triplet	8.0-8.4 Multiplet	5.76 Multiplet
$-(\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n-$	-	-	7.68 Triplet	8.1-8.7 Multiplet	5.93 Triplet

^a Proton magnetic resonance spectra were determined with a Varian HA-100 D-15 NMR spectrometer operating in the HA-field sweepmode. Chemical shifts are reported on the τ scale with tetramethylsilane ($\tau = 10.00$) as an internal standard. Spectra were obtained from deuteriochloroform solutions.

TABLE 4. Thermal Stability of Poly- ϵ -caprolactone as Function of Carboxyl Content [36]

Sample No.	\bar{M}_n	Acid No. (mg KOH/g polymer)	Thermal treatment ($^{\circ}$ C/1 hr)	Melt flow ratio ^a
1	20,000	0.40	220	2.2
2	20,000	1.20	220	3.6
3	20,000	1.80	220	5.3
4	20,000	1.80	220	13.5

^aSee footnote b of Table 2 for definition of melt flow ratio.

TABLE 5. Ambient Temperature Stability of Poly- ϵ -caprolactone as a Function of Carboxyl Content [36]

Sample No.	Acid No. (mg KOH/g polymer)	Reduced viscosity ^a (initial)	Time (t) at ambient temp (months)	Reduced viscosity ^a at t	Change in reduced viscosity
1	0.9	0.67	12	0.65	0.02
2	1.2	0.98	24	0.51	-
3	1.9	0.75	10	0.64	0.11
4	1.9	0.62	10	0.50	0.12
5	2.2	0.64	12	0.52	0.12

^aReduced viscosity, 0.2 g/dl in benzene at 30 $^{\circ}$ C.

density had a value of 1.17 g/cm³ which compares favorably with the measured value [41] of 1.146 g/cm³. Poly- ϵ -caprolactone melts at 63 $^{\circ}$ C which is markedly less than the 136 $^{\circ}$ C melting point of polyethylene. The large difference in these melting points has been explained in terms of entropy [40]. There is a greater degree of rotational freedom about the chain backbone in the case of the lactone polymer which leads to a significantly higher entropy of fusion compared to polyethylene. This effect apparently is more than sufficient to overcome the increased polarity of the polyester compared to

TABLE 6. ϵ -Caprolactone Polymers and Copolymers of High Thermal Stability

Sample No.	\overline{M}_n or reduced viscosity ^a	C/1 hr	Melt flow ratio ^b
Poly- ϵ -caprolactone			
1	5,000	250	1.2
2	10,000	220	1.1
3	10,000	250	1.0
4	20,000	220	1.5
ϵ -Caprolactone—Ethylene Oxide Block Copolymer			
5	0.30	250	1.3
6	0.40	250	1.2

^aReduced viscosity measured at 0.2% polymer in benzene at 30°C.

^bSee footnote b of Table 2 for definition of melt flow ratio.

TABLE 7. Ambient Temperature Stability^a

\overline{M}_n	Reduced viscosity (initial)	Time (t) at ambient temp (months)	Reduced viscosity at t	Change in reduced viscosity
~20,000	0.70	12	0.72	+0.02
~20,000	0.67	12	0.65	-0.02
~10,000	0.29	18	0.30	+0.01

^aG. L. Brode and L. A. Pilato, previously unreported data.

polyethylene. Our studies have shown that both polymers crystallize very readily and cannot be quenched to glasses [42] whereas certain other lactone polymers can be glassified by a quenching process [43].

In general, high molecular weight poly- ϵ -caprolactone may be classified as a tough, crystalline polymer of moderate melting point. Physical properties of the material are given in Table 8 [41].

TABLE 8. Physical Properties of High Molecular Weight Poly- ϵ -caprolactone at Ambient Conditions [41]

\bar{M}_w (light scattering)	40,000
1% Secant modulus (psi)	50,000
Elongation (%)	~750
Yield stress (psi)	1,600
Tensile strength (based on initial cross-sectional area) (psi)	3,500
Melting Point ($^{\circ}\text{C}$) [40]	63
Glass transition temperature, 1 Hz	
Partially crystalline ($^{\circ}\text{C}$)	-60
Amorphous ($^{\circ}\text{C}$) [42]	-71
Density (g/cc) 20 $^{\circ}\text{C}$	1.149
30 $^{\circ}\text{C}$	1.143
62 $^{\circ}\text{C}$	1.069
From 30 to -30 $^{\circ}\text{C}$ (add)	5.6×10^{-4}
From 62 to 100 $^{\circ}\text{C}$ (add)	-6.8×10^{-4}
Equilibrium moisture content (%)	
50% Relative humidity	0.07
100% Relative humidity	0.43

At weight-average molecular weights of less than about 25,000 the polymer is hard and brittle and similar tensile properties cannot be measured.

The electrical properties of the above-described, high molecular weight poly- ϵ -caprolactone are given in Table 9 [44]. In a general sense these would be called good over-all electrical properties. In particular, volume resistivity is about 10^{11} Ω/cm , which is about four orders of magnitude lower than that of most other polymers and is comparable to values found for nitrocellulose and phenol-formaldehyde polymers [45].

DILUTE SOLUTION PROPERTIES

The hydrodynamic properties and unperturbed dimensions of fractionated poly- ϵ -caprolactone have been studied [46]. The polymer used was prepared by a bulk process using dibutylzinc as

TABLE 9. Electrical Properties of Poly- ϵ -caprolactone [44]

\bar{M}_w (light scattering)	40,000
Dielectric strength (V/mil)	
Short time	237
Step by step	237
Dielectric constant (Hz)	
60	4.31
10^3	4.28
10^6	4.23
Dissipation factor (Hz)	
60	0.0321
10^3	0.0035
10^6	0.0050
Volume resistivity (23°C, 50% relative humidity) (Ω/cm)	4.76×10^{11}
Arc resistance (time to carbonize) (sec.)	138

the catalyst (Type 2, Table 1). Weight-average molecular weights were determined from sedimentation velocity experiments and correlated with the intrinsic viscosity determined in dimethyl formamide and in benzene at 30°C. These data were expressed as follows:

$$[\eta] = 1.91 \times 10^{-4} \bar{M}_w^{0.73} \quad (\text{DMF}) \quad (17)$$

and

$$[\eta] = 9.94 \times 10^{-5} \bar{M}_w^{0.82} \quad (\text{Benzene}) \quad (18)$$

The average sedimentation coefficient S° determined in benzene at 30°C was described by

$$S^\circ = 3.58 \times 10^{-15} \bar{M}_w^{0.39} \quad (19)$$

By using extrapolation techniques, it was found that the solution properties of the polymer under theta conditions could be described by

$$[\eta]_\theta = 1.1 \times 10^{-3} \bar{M}_w^{0.5}$$

The steric hindrance parameter σ had the low value of 1.37. Since this parameter, which is the ratio of the unperturbed mean-square end-to-end distance calculated from K_θ to the corresponding dimension calculated for the free rotation model of a polymer chain, is low, it indicates the poly- ϵ -caprolactone molecule is a very flexible coil.

It is interesting to note that the first fraction obtained in the study [46] appeared to be anomalous in certain characteristics. The thought was that the anomaly was due to the presence of substantial amounts of catalyst residue, and elemental analysis confirmed that the catalyst was associated with this fraction. A later dialysis study [6] of a similar polymer prepared with dibutylzinc indicated the presence (1.2%) of a low molecular weight fraction ($\bar{M}_n = 740$) in the polymer. Elemental analysis of this material indicated that it contained about 15% of the zinc added to the system as a catalyst, suggesting that much of the catalyst may be associated with a low molecular weight species. It was not known if this fraction had been terminated in the early stages of the polymerization or if it represented a very slow rate of polymerization in the early stages of the reaction. Although it is speculation, it is possible that the reason for the presence of the catalyst in this fraction is that it is part of an insertion reaction product of the organometallic and ϵ -caprolactone. Thus this material could have been selectively precipitated with the first fraction of the earlier study [46].

POLY- ϵ -CAPROLACTONE-POLYMER BLENDS

Poly- ϵ -caprolactone is of major interest because it has a unique ability to blend with a variety of other polymers over wide composition ranges. The materials that result when such blends are made have useful properties. The studies that have been made indicate that three types of blends result when poly- ϵ -caprolactone is combined with other polymers. These types are 1) a crystalline interaction, 2) a true compatibility in which the blend exhibits a single glass transition, and 3) a mechanical compatibility, but also without a serious alteration of properties and often improvements in selected properties. The mechanically compatible systems exhibit two glass transitions. One of these glass transition is indicative of poly- ϵ -caprolactone and the other is related to the other homopolymer in the blend.

Crystalline Polymer Blends

It has been found that a crystalline interaction exists when poly- ϵ -caprolactone is blended with a polyolefins such as polyethylene and

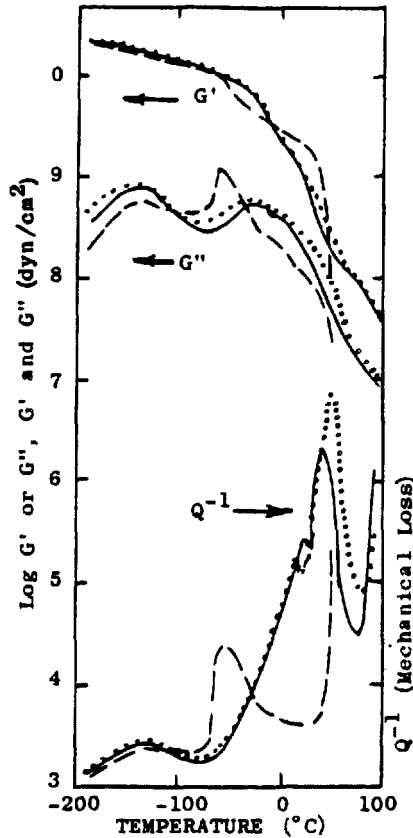


FIG. 1. Dynamic mechanical properties of low-density polyethylene (—), quenched poly- ϵ -caprolactone (- -) [42], and a 90/10 blend of these two polymers (. . .).

polypropylene [47]. Figure 1 is a plot of the dynamic mechanical properties of low-density polyethylene, poly- ϵ -caprolactone, and a 90/10 blend of the two polymers. Addition of the polylactone to polyethylene apparently has affected only the alpha relaxation of polyethylene. This transition is usually hypothesized as being related to vibrational or reorientational motion in the crystals of polyethylene [48]. In this case, the blend has a relaxation maximum that is comparable to that of the alpha relaxation in polyethylene except that it occurs at a higher temperature and is larger in

magnitude. Thus it would appear that the crystalline interaction that occurs between polyethylene and polycaprolactone restricts the motion within the polyethylene crystallites, for a higher temperature is required for the relaxation to take place. It is interesting to note that the lactone polymer does not give a visible glass transition in the blend. This may be due to the nature of the crystalline interaction or to the fact that the amount of amorphous polycaprolactone which would give rise to a glass transition temperature is small.

Compatible Polymer Blends

It is well known that it is difficult to blend polymers and obtain compatibility. For true compatibilization to take place, ΔF must be negative in the thermodynamic expression $\Delta F = \Delta H - T\Delta S$. Mixing is usually an endothermic process, and the enthalpic change is expected to be positive and not in favor of mixing. The entropic change would be positive, and it would be in favor of mixing. However, this change is small due to the relatively small number of molecules involved when one deals with polymers. In fact, it is these arguments that led Flory [49] to make the statement "incompatibility of chemically dissimilar polymers is observed to be the rule and compatibility is the exception." Since polycaprolactone is truly compatible with a number of different polymers, it stands out as unique in blending ability.

Poly- ϵ -caprolactone has been found to be compatible with poly(vinyl chloride), nitrocellulose, Union Carbide Corporation's Phenoxy A [poly(hydroxyether) from the condensation of bisphenol A and epichlorohydrin], Hercules' Penton (a chlorinated polyether), styrene/acrylonitrile copolymer, and polyepichlorohydrin. In the case of poly(vinyl chloride), it has been shown [42] that these blends have glass transition temperatures (T_g) that extrapolate to a value of -71°C for the glass transition temperature of amorphous poly- ϵ -caprolactone. This value of T_g is 16 degrees lower than the value obtained for the polymer when it is molded and aged a few days at room temperature, and 11 degrees lower than is obtained for the polymer quenched from the melt into liquid nitrogen. The value of -71°C will be used as the basis for extrapolations made in these studies.

As another example of a compatible system, blends of polycaprolactone and nitrocellulose may be considered. In this system the lactone polymer acts as a polymeric plasticizer. As the polycaprolactone content is increased the modulus decreases and the elongation increases. The change in elongation as a function of plasticizer content is shown in Fig. 2 for an 11% nitrogen content

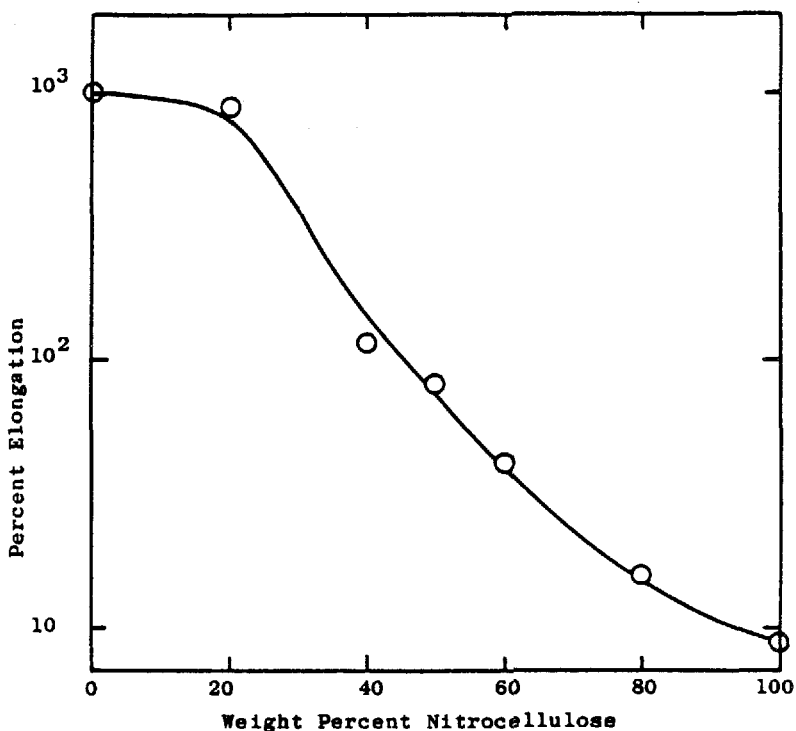


FIG. 2. Elongation of nitrocellulose/poly- ϵ -caprolactone blends as a function of nitrocellulose content (1/2 sec nitrocellulose, 11% nitrogen, D.S. = 2.0).

(D.S. \sim 2.0) nitrocellulose. Films of the blends cast from isopropanol and typical solvents such as 2-nitropropane are clear and have high gloss, improved reverse impact resistance, and improved sunlight resistance over nitrocellulose alone. When the blends contain less than 50% nitrocellulose, they become hazy after a time due to crystallization of a portion of the polycaprolactone.

It is known that the behavior of plasticized nitrocellulose is complicated by crystallinity [50]. In studying the dynamic mechanical properties of these blends with a torsion pendulum [51] at a frequency of about 1 Hz, a rather complicated behavior was found. Apparently this behavior was due to crystallinity effects which were quite pronounced when more than 50% nitrocellulose was present.

An attempt to circumvent the crystallinity problem was made by studying blends in which the nitrocellulose content was less than 50% and studying the properties of such blends in the quenched state. The blends were made by dissolving a 12% nitrogen content (D.S. ~2.3) nitrocellulose and polycaprolactone in a mixture of isopropanol and n-propyl acetate. After solvent removal, the films were compression molded into plaques. Then before the properties of the blends were examined, each specimen was warmed to about 120°C. This temperature was well above the point at which the specimens became clear. Each blend was then quenched from the heated state into liquid nitrogen and loaded into the precooled (-190°C) chamber of the torsion pendulum. All blends remained transparent after this process.

The real or storage component of the complex shear modulus G' is shown in Fig. 3. In each case at T_g or the point of marked modulus change increased as the nitrocellulose content increased, indicating the polycaprolactone was acting as a plasticizer. However, it is interesting to note that those blends containing 25% or less nitrocellulose underwent an increase in modulus above the glass transition. For clarity the entire G' curve is shown only for the 90/10 blend. The arrow indicates that the 83/17 and 75/25 blends underwent a similar modulus increase. This modulus increase is due to a devitrification of the blend and a crystallization, presumably of the polycaprolactone. The imaginary or loss component of the complex shear modulus for these blends is shown in Fig. 4. The relaxation maxima at -135°C are due to the five-membered methylene sequence in polycaprolactone and the major peak is the T_g . Another relaxation peak or shoulder is apparent at -80 to -90°C at the higher nitrocellulose contents and may be ascribed to a secondary motion in the nitrocellulose.

The values of T_g taken from G'' and from mechanical loss Q^{-1} are shown in Fig. 5. It is expected that the value of T_g from G'' will be two to three degrees less than the value from Q^{-1} [52]. It is readily apparent that this is true only for the very low nitrocellulose content blends. For the 50/50 blend there is a 32-degree difference in T_g as measured by these two parameters. It is thought that this difference is due to crystallinity of nitrocellulose and that the values of T_g taken from G'' are more representative of the actual T_g [42]. The values of T_g for these blends and for higher nitrocellulose content blends are tabulated in Table 10. In each case T_g was taken to be the relaxation peak that was greatest in magnitude in the property-temperature spectrum. These figures show that both T_g and the difference in T_g as measured by G'' and Q^{-1} change in a

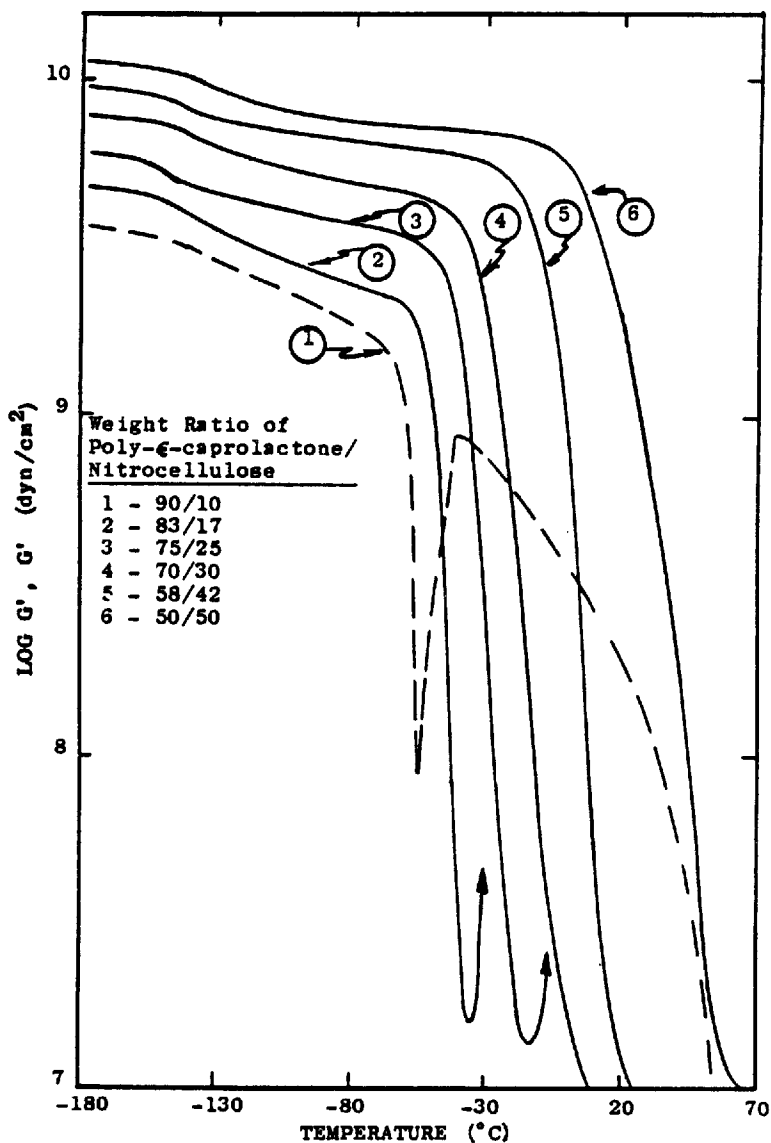


FIG. 3. Real component of the complex shear modulus G' for poly- ϵ -caprolactone/nitrocellulose blends. For clarity all curves except that for the 50/50 blend are displaced vertically from each other. All specimens were warmed to 120°C and quenched into liquid nitrogen.

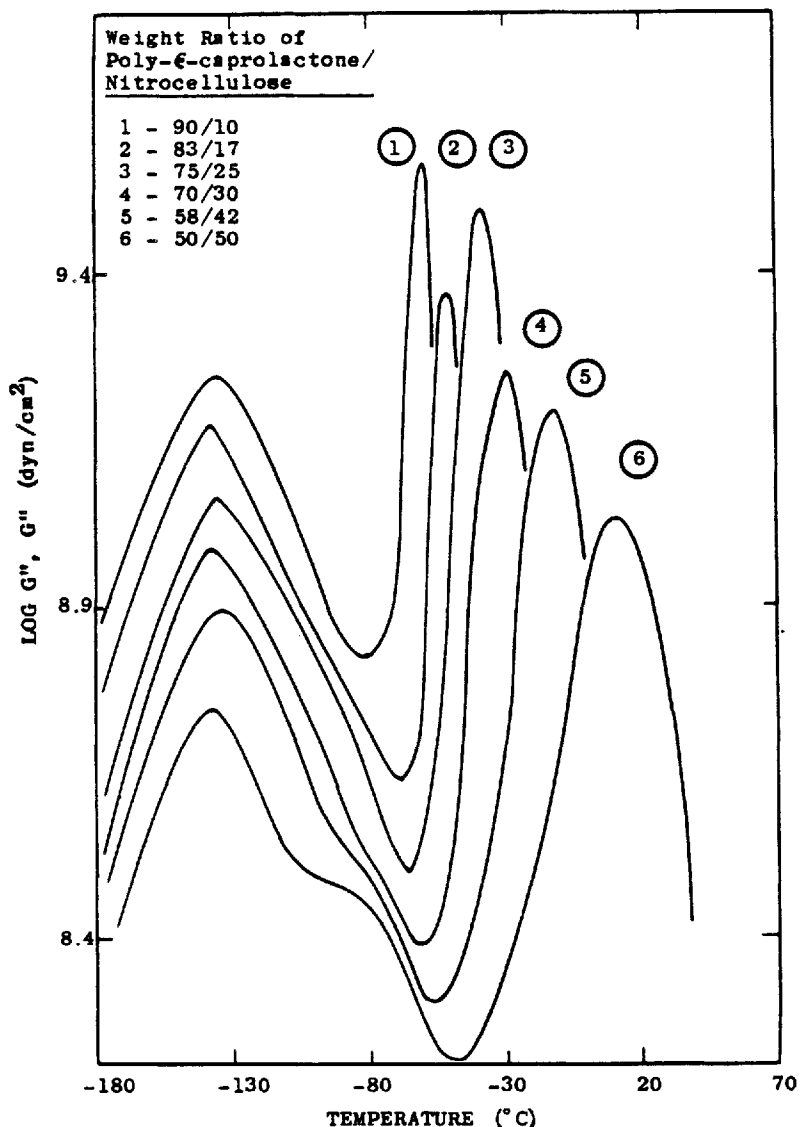


FIG. 4. Loss component of the complex shear modulus G'' for poly- ϵ -caprolactone/nitrocellulose blends. For clarity all curves except that for the 50/50 blend are displaced vertically from each other. All specimens were warmed to 120°C and quenched into liquid nitrogen.

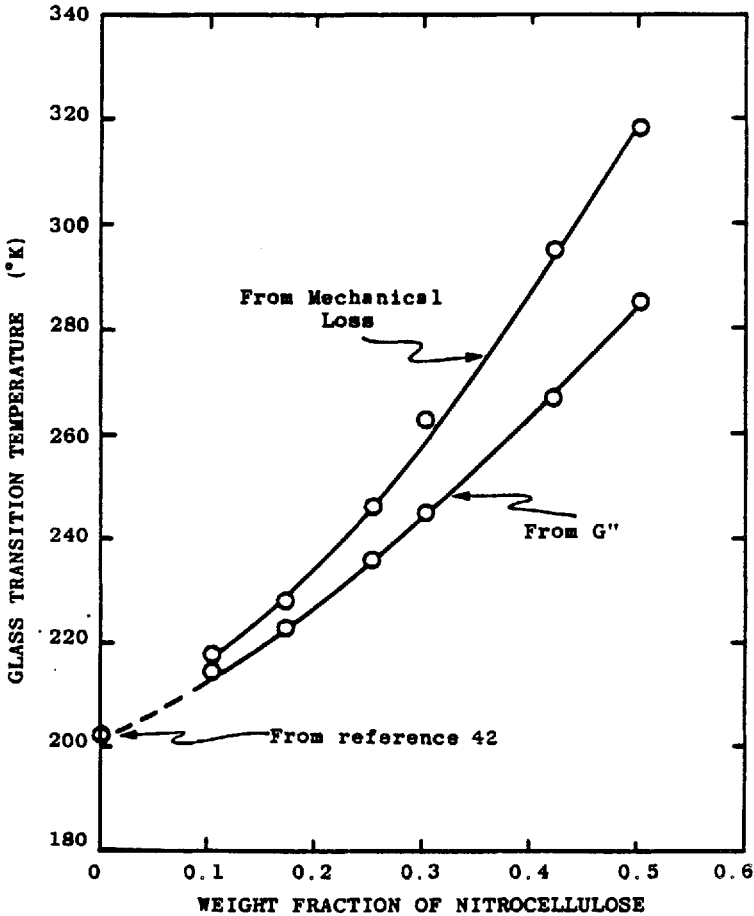


FIG. 5. Glass transition temperature as a function of nitrocellulose content for blends of poly- ϵ -caprolactone and nitrocellulose.

rather regular manner until more than 50% nitrocellulose is in the blend. At higher nitrocellulose contents T_g from Q^{-1} has a fairly regular pattern, but T_g from G'' decreases rather than increases in the 70-80% nitrocellulose range. No explanation can be given for this behavior.

TABLE 10. Glass Transition Temperature of Nitrocellulose (12% Nitrogen)/Poly- ϵ -caprolactone Blends^a

Weight fraction		Glass transition temperature ($^{\circ}\text{C}$)		Difference in T_g from G'' and Q^{-1} ($^{\circ}\text{C}$)	Other relaxations apparent in G'' ($^{\circ}\text{C}$)
Poly-caprolactone	Nitro-cellulose	G''	Q^{-1}		
1.00	0.00	-71 [42]	-	-	-135
0.90	0.10	-58	-55	3	-135
0.83	0.17	-50	-45	5	-135
0.75	0.25	-37	-27	10	-95, -135
0.70	0.30	-28	-10	18	-85, -135
0.58	0.42	-5	+12	17	-85, -135
0.50	0.50	+12	+45	33	-85, -135
0.41	0.59	+17	+40	23	-85, -135
0.30	0.70	+5	+65	60	-85, -135
0.20	0.80	-5	+80	85	-90, -135
0.10	0.90	72	+120	48	-15, -85, -135
0.00	1.00 ^b	115	+120	5	-10, -75, -110

^aSpecimens were quenched from 120°C into liquid nitrogen.

^bData obtained on a cast film that was not quenched.

Polycaprolactone and Phenoxy also form compatible polymer blends. Phenoxy is a poly(hydroxyether) prepared by the condensation of bisphenol-A and epichlorohydrin. Blends of these two polymers were prepared on a two-roll mill, and plaques of the blends were prepared by compression molding the milled polymers. Those blends that contain more than 50% polycaprolactone will undergo a stiffening and hazing due to polycaprolactone crystallinity after a few days at room temperature. For this reason such blends were studied in a quenched state. Figure 6 is a plot of blend T_g as a function of Phenoxy concentration. Here the glass transition temperature increases regularly as the Phenoxy content is increased. In addition, as shown by the solid line in Fig. 6, when -71°C is taken as T_g of polycaprolactone [42] and 103°C as the T_g of Phenoxy, the data are well fit by the Fox

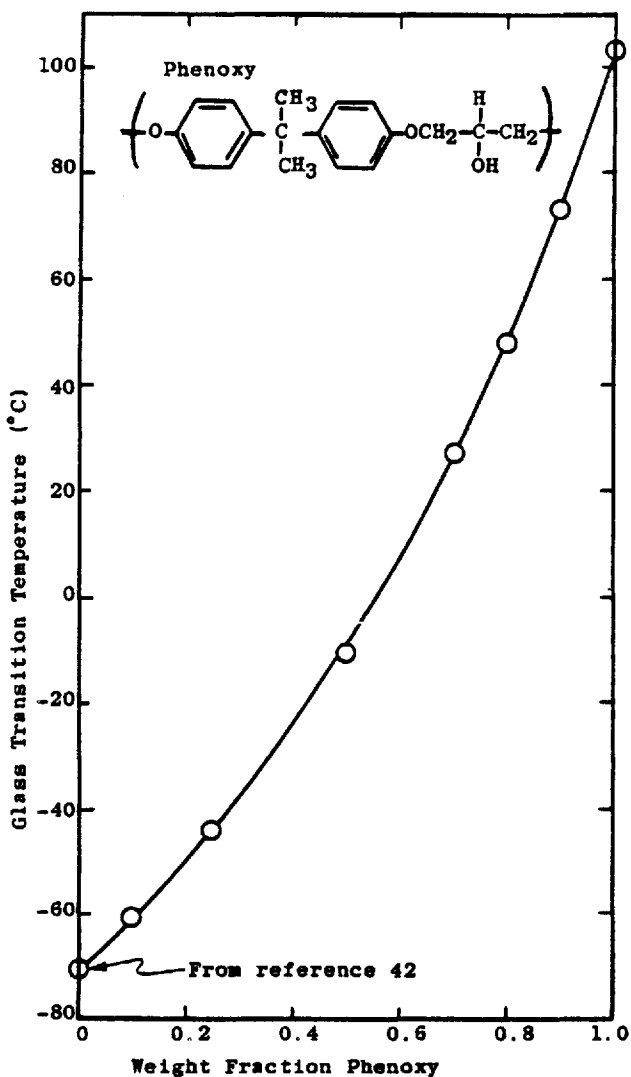


FIG. 6. Glass transition temperature from G'' as a function of phenoxo content for blends of poly- ϵ -caprolactone and phenoxo. The solid line is the Fox equation, $(1/T_{g1,2}) = (w_1/T_{g1}) + (w_2/T_{g2})$. $T_{g1} = -71^\circ\text{C}$ and $T_{g2} = 103^\circ\text{C}$.

expression [53], $(1/T_{g1,2}) = (W_1/T_{g1}) + (W_2/T_{g2})$. In this expression, W is the weight fraction of a particular component, the subscripts 1 and 2 refer to the two homopolymers, and 1,2 refer to the blend. Thus one can conclude that these are compatible blends, though the blends containing more than 50% polycaprolactone are completely compatible only for the time scale necessary to make measurements.

Polyepichlorohydrin is also compatible with polycaprolactone. These blends show phase separation at high levels of polycaprolactone, but at the 20 to 30% polycaprolactone level these blends are compatible for extended periods of time. Figure 7 is a plot of G'' as a function of temperature for polyepichlorohydrin and for two blends of this polymer with polycaprolactone. Here we find that the T_g decreases as the lactone polymer concentration is increased.

To obtain these data, the blends were made by hot melt blending the polymers. But, they were not quenched into liquid nitrogen after compression molding. However, in the case of the 50/50 blend, the blend was prepared, a specimen was molded, and then within a few minutes it was loaded into the testing device. Since cooling is quite rapid in the instrument, the blend was given a minor quench. As can be seen in Fig. 8, the 50/50 blend exhibited a modulus increase due to devitrification above the T_g . However, the devitrification was not rapid, for the modulus increase is less sharp in comparison to that experienced with the nitrocellulose blends discussed above.

The data given in Table 11 describe what happens when this system is aged. The experimental T_g values agree quite well with values calculated from the Fox expression when the value of -71°C of amorphous polycaprolactone is used. However, when the blends are aged for 10 days at room temperature, there is no change in T_g of the 10% blend, but there is a marked change in T_g of the 50% blend. This latter blend becomes translucent as time passes. The translucency is due to crystallization of a portion of the polycaprolactone, since warming at about 60°C (the melting point of this polymer) for a few minutes returns the specimen to a transparent state. Of course, the polycaprolactone that has not crystallized remains compatible with the polyepichlorohydrin.

Mechanically Compatible Blends

The next example is of an incompatible polymer blend in that two glass transition temperatures are obtained. However, these blends would be classified as being mechanically compatible, for the mechanical properties of the materials are not what would be

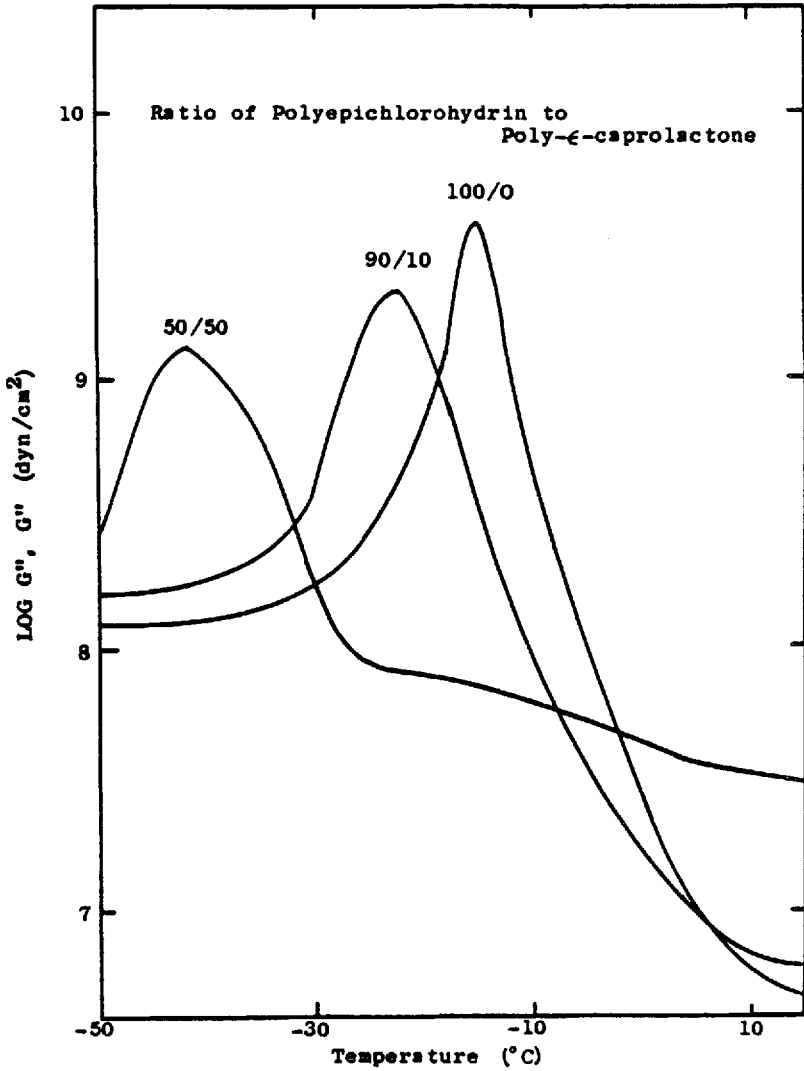


FIG. 7. Loss component of the complex shear modulus as a function of temperature for polyepichlorohydrin/poly- ϵ -caprolactone blends.

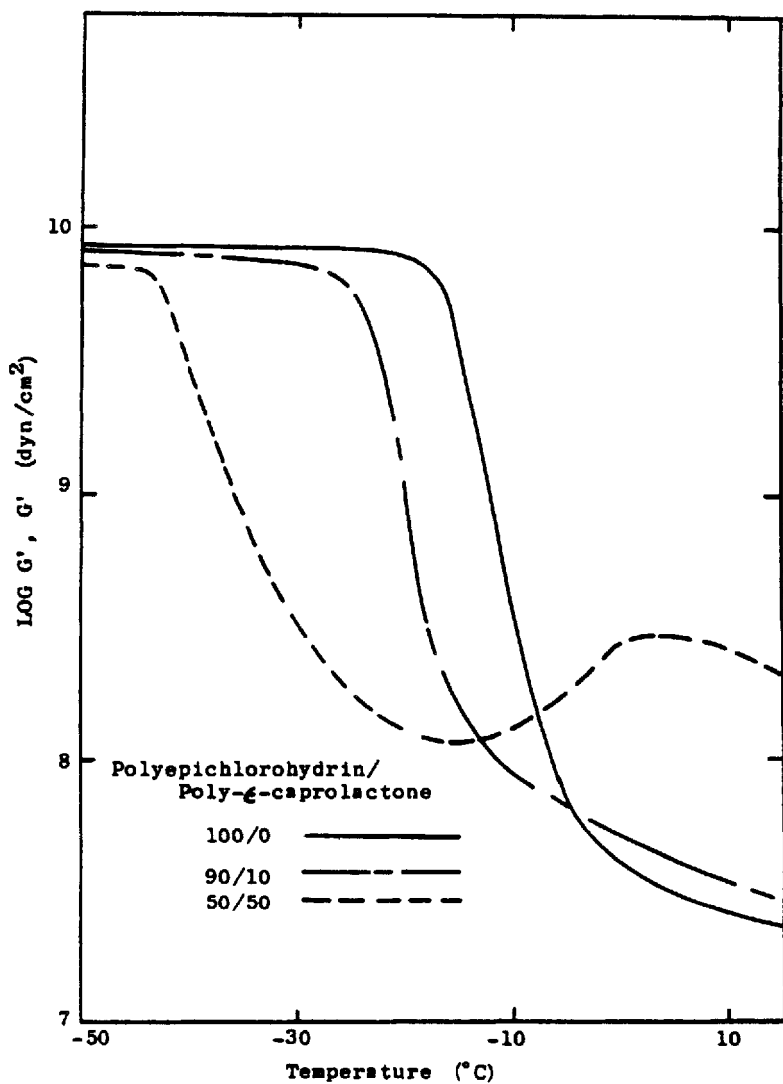


FIG. 8. Storage component of the complex shear modulus as a function of temperature for polyepichlorohydrin/poly- ϵ -caprolactone blends.

TABLE 11. Glass Transition Temperatures for Polyepichlorohydrin/Polycaprolactone Blends

Per cent PCL	Glass transition temperature	
	Experimental, G'' ($^{\circ}\text{C}$)	Calculated ^a ($^{\circ}\text{C}$)
0	-15	-
10	123	-22
50	-42	-47
90	-52	-57
Aged 10 Days at Room Temperature		
0	-15	-
10	-23	-
50	-30	-

$$a_{1/T_{g1,2}} = w_1/T_{g1} + w_2/T_{g2}; T_{g1} = 202^{\circ}\text{K}, \left(\text{C} \begin{array}{c} \text{---} \text{C} \text{---} \text{O} \\ | \\ \text{CH}_2\text{Cl} \end{array} \right)_n$$

expected of a truly incompatible system. Polycaprolactone and poly(vinyl acetate) were melt blended on a two-roll mill. As shown in Fig. 9, the glass transition temperature of each of the homopolymers is apparent in G'' . As the polycaprolactone content is increased, the magnitude of its relaxation maximum at about -60°C is increased. In addition, the relaxation maximum at 30 to 40°C due to the poly(vinyl acetate) is apparent in both blends. Thus, since the characteristic T_g peaks of each homopolymer do not disappear, it must be concluded that the domain size of each of the mixed polymers is greater than a 10 - 30 \AA size [54] required for true compatibility. Yet, these blends and others do have good physical properties as shown in Table 12. The modulus and tensile strength decrease and the elongation increases as the polycaprolactone content is increased. Such behavior is indicative of a plasticized system. In addition, the tensile strengths of the blends are of sufficient magnitude to show that the blends have good mechanical properties. Thus one may conclude that although the blends are incompatible in the usual sense, there must be sufficient interaction of the polymers on a large domain size basis that good mechanical properties are obtained. Somewhat similar

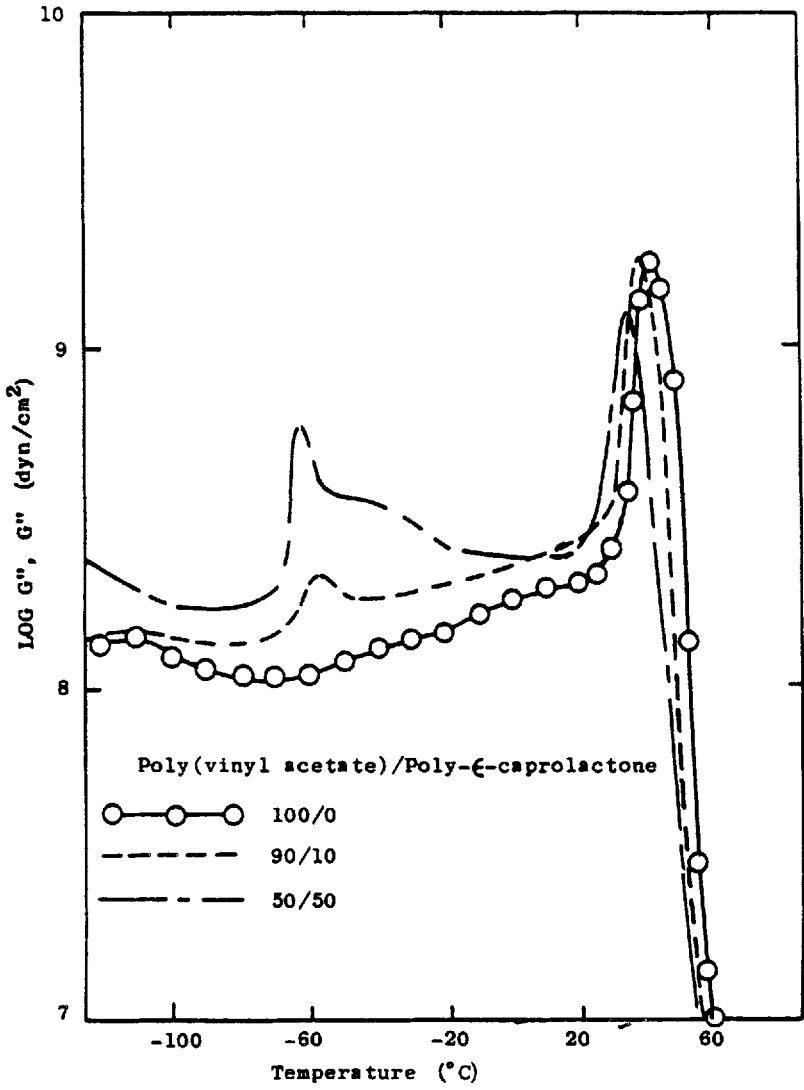


FIG. 9. Loss component of the complex shear modulus as a function of temperature for poly(vinyl acetate)/poly- ϵ -caprolactone blends.

TABLE 12. Tensile Properties^a of Polycaprolactone/Poly(vinyl Acetate) Blends^b

Weight fraction		1% Secant modulus (psi)	Tensile strength (psi)	Per cent elongation
Polycaprolactone	Poly(vinyl acetate)			
0.00	1.00	200,000	5,200	8
0.01	0.99	190,000	4,500	8
0.10	0.90	180,000	4,900	6
0.20	0.80	67,000	3,300	670
0.30	0.70	70,000	3,200	680
0.40	0.40	60,000	3,000	740
0.50	0.50	22,000	3,400	1,200
0.90	0.10	22,000	6,100	1,600

^aProperties were determined with an Instron tester on 1/4-in. wide rectangular strips. Elongation was taken as measured extension rather than between fiduciary marks.

^bCompression molded test specimens.

behavior has been shown for blends of polycaprolactone and either polystyrene or poly(methyl methacrylate).

UTILITY OF POLY- ϵ -CAPROLACTONE

The ability of polycaprolactone to blend with other polymers can be used in several ways [41]. For example, when it is added to polypropylene or polyethylene, melt spun fibers that are dyeable with disperse dyestuffs and with excellent physical properties are produced. It can act as an adhesive for polymer films of the same or different composition. It is an excellent low-profile additive for fiber glass reinforced polyester systems. It improves the impact strength of ABS and of impact polystyrene. The polymer is an effective pigment dispersant. It has improved the gloss of extruded thermoplastics and the stress crack resistance of polyethylene.

Low Profile Additive

At fairly low levels, polycaprolactone produces excellent low profile surfaces in both "premix" and "preform" polyester resins.

TABLE 13. Properties of Preform Unsaturated Polyesters Containing Various Low Profile Additives [41, 55]

Formulation (molded 2 min, 275°C, 500 psig)					
36.5 parts 3.0/1.0/4.4 mole ratio of maleic anhydride/phthalic anhydride/propylene glycol plus 30% by weight styrene					
12.0 parts low profile additive (40% styrene solution)					
20.8 parts filler (Al-Sil-Ate LO)					
30.2 parts glass mat					
0.15 parts Lapersol 256					
0.25 parts Zelec Un					
Low profile additive	MCR ^a μin./in.	Gloss ^b	Paint adhesion ^c	Reverse impact resistance ^d	Mold release character ^b
None	1200	Poor	Excellent	2	Excellent
Polycaprolactone	170	Excellent	Excellent	12	Excellent
Poly(vinyl chloride)	180	Good	Poor	3	Poor
Polyethylene	180	Good	Poor	3	Fair
Poly(methyl methacrylate)	170	Good	Poor	3	Poor

^aMeasured with a Microcorder, Bendix Corp.

^bVisual observation.

^cCrosshatch adhesion.

^dDistance of drop (inches) required for a 1/2-lb steel ball to cause failure in a 100-mil panel.

As shown in Table 13, the preform system containing polycaprolactone is characterized by a low-profile surface (low MCR value), an excellent gloss, paint adhesion, and mold release, and a markedly improved reverse impact resistance [41, 55]. Although the other low profile additives such as poly(vinyl chloride), polyethylene, and poly(methyl methacrylate) result in good surface smoothness, they do not provide the outstanding properties imparted by polycaprolactone.

Adhesive

Polycaprolactone also acts as an adhesive polymer which can be used to bond various substrates to each other. Peel strengths of the

TABLE 14. Bond Strengths Obtained When Polycaprolactone is Used as an Adhesive for Various Substrates [44]

Substrate	Bonding parameters			Peel strength (lb/in.) ASTM-D 1876
	Temperature (°C)	Pressure (psi)	Time (min)	
ABS terpolymer	150	80	2	> 7
Glass	200	1	15	5
Glass reinforced epoxy board	150	20	2	>30
Impact polystyrene	150	40	2	> 5
Paperboard	100	10	1	Paper failure
Plywood	180	20	3	2, Wood failure
Polyurethane	185	20	2	8
Poly(vinyl chloride)	170	20	3	>25
70/30, Poly(vinyl chloride)/dioctyl- phthalate	165	30	3	>28

adhesive bond formed by heat and pressure are listed in Table 14 [44]. Since the polymer is soluble in a number of common solvents such as benzene, toluene, chloroform, methylene chloride, 2-nitropropane, 1,4-dioxane, and tetrahydrofuran, it should be possible to make adhesive solutions or printing inks from polycaprolactone or blends of polycaprolactone with nitrocellulose or other polymers. Of course, the melting point of the polymer would represent the upper temperature use limit when it is used alone.

REFERENCES

- [1] R. D. Lundberg and E. F. Cox, Ring Opening Polymerization, Vol. 2 (K. C. Frisch and S. L. Reegen, eds.), Dekker, New York, 1969, pp. 247-302.
- [2] Japanese Patent 5910 (1968), to Asahi Chemical Industries Co. Ltd.
- [3] K. Saotome and Y. Kodaira, Makromol. Chem., **82**, 41 (1965).
- [4] D. R. Wilson and R. G. Beaman, J. Polym. Sci., Part A-1, **8**, 2161 (1970).

- [5] T. L. Gresham et al., J. Amer. Chem. Soc., **73**, 3168 (1951).
- [6] R. D. Lundberg, J. V. Koleske, and K. B. Wischmann, J. Polym. Sci., Part A-1, **7**, 2915 (1969).
- [7] Belgium Patent 743123 (1970) to Union Carbide Corp.
- [8] E. F. Cox and F. Hostettler, U.S. Patent 3,021,310 to Union Carbide Corp.
- [9] U.S. Patent 3,476,715 (1969) to DuPont and Company.
- [10] French Patent 1,487,200 (1967) to Kanegafuchi Spinning Co., Ltd.
- [11] Japanese Patent 26629 (1968) to Nippon Rayon Co., Ltd.
- [12] U.S. Patent 3,169,945 (1965) to Union Carbide Corp.
- [13] U.S. Patent 3,284,417 (1966) to Union Carbide Corp.
- [14] U.S. Patent 2,890,208 (1959) to Union Carbide Corp.
- [15] Netherlands Appl. 6,608,706 (1967) to Shell International Research Maatschappi, N.V.
- [16] H. Cherdron, H. Ohse, and F. Korte, Makromol. Chem., **56**, 179 (1962).
- [17] Y. Yamashita, J. Tsuda, M. Okada, and S. Ivatsuki, J. Polym. Sci., Part A-1, **4**, 2121 (1966).
- [18] K. Itoh, S. Sakai, and Y. Ishii, J. Org. Chem., **31**, 3948 (1966).
- [19] K. Itoh, S. Sakai, and Y. Ishii, Tetrahedron Lett., **1966**, 4941.
- [20] K. Itoh et al. J. Organometal. Chem., **10**, 451 (1967).
- [21] J. G. Noltes, F. Verbeek, H. G. J. Overmars, and J. Boersma, J. Organometal. Chem., **24**, 257 (1970).
- [22] T. Hirabayashi, K. Itoh, S. Sakai, and Y. Ishii, J. Organometal. Chem., **25**, 33 (1970).
- [23] U.S. Patent 3,308,155 (1967) to Continental Oil Co.
- [24] W. McMahon et al., J. Chem. Eng. Data, **4**, 57 (1959).
- [25] D. A. S. Ravens and J. M. Ward, Trans. Faraday Soc., **57**, 150 (1961).
- [26] G. L. O' Connor and H. R. Nace, J. Amer. Chem. Soc., **75**, 2118 (1953).
- [27] D. H. R. Barton, A. J. Head, and R. J. Williams, J. Chem. Soc., **1953**, 1715.
- [28] A. T. Blades, Can. J. Chem., **32**, 366 (1954).
- [29] E. E. Sommers and J. I. Crowell, J. Amer. Chem. Soc., **77**, 5443 (1955).
- [30] J. Gomory, O. Mlijnek, and J. Stimel, J. Polym. Sci., **59**, 71 (1962).
- [31] F. Farre-Rues et al., Bull. Soc. Chim., **1965**, 455.
- [32] I. F. Goldfarb and R. McGuchan, U.S. Govt. Rep. AFML-TR-68-182, Part 1, 1968.
- [33] I. F. Goldfarb and R. McGuchan, Ibid., Part 2, 1969.
- [34] D. M. Young, F. Hostettler, L. C. Shriver, and R. W. McLaughlin, Amer. Chem. Soc., Div. Paint, Plastics and Printing Ink Chem., **16**(3), 108 (Sept. 1956).

- [35] I. S. Megna and A. Koroscil, J. Polym. Sci., Part B, 6, 653 (1968).
- [36] G. L. Brode and L. A. Pilato, Union Carbide Corp., previously unpublished results.
- [37] G. L. Brode, J. H. Lauterbach, and J. Lewis, Union Carbide Corp., previously unpublished results.
- [38] D. Horton and J. H. Lauterbach, J. Org. Chem., 34, 86 (1969).
- [39] J. H. Lauterbach, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, Dec. 1970, and references cited therein.
- [40] H. Bittiger, R. H. Marchessault, and W. D. Niegisch, Acta Cryst., B26, 1923 (1970).
- [41] Union Carbide Corp. Bulletin F-42501, New Polycaprolactone Thermoplastic Polymers, PCL-300 and PCL-700, 1969.
- [42] J. V. Koleske and R. D. Lundberg, J. Polym. Sci., Part A-2, 7, 795 (1969).
- [43] J. V. Koleske and R. D. Lundberg, J. Polym. Sci., 10, 323 (1972).
- [44] W. A. Smarook, Union Carbide Corporation, Unpublished Data, 1969.
- [45] Modern Plastics Encyclopedia, 47(10A) 767 (October 1970).
- [46] J. V. Koleske and R. D. Lundberg, J. Polym. Sci., Part A-2, 7, 897 (1969).
- [47] E. R. Walter and J. V. Koleske, Gen. Offen. 2,015,262; Chem. Abstr., 74, 43456y (1971).
- [48] N. G. McCrum, B. E. Read, and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, New York, 1967, p. 358.
- [49] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York, 1953, p. 555.
- [50] K. Ninomiya and J. D. Ferry, J. Polym. Sci., Part A-2, 5, 195 (1967).
- [51] L. E. Nielsen, Rev. Sci. Instrum., 22, 690 (1951).
- [52] P. R. Pinnock and I. M. Ward, Proc. Phys. Soc., 81, 260 (1963).
- [53] T. G. Fox, Bull. Amer. Phys. Soc., 2, 123 (1956).
- [54] C. F. Hammer, Macromolecules, 4(1), 69 (1971).
- [55] L. R. Comstock and P. L. Smith, Union Carbide Corporation, Unpublished Data, 1969.

Accepted by editor September 15, 1971

Received for publication October 28, 1971