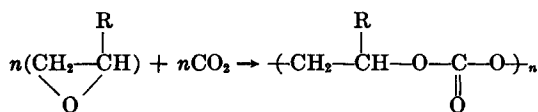


NOTES

***Poly(ethylene Carbonate) and Poly(propylene Carbonate):
Transitions and Thermomechanical Spectra***

INTRODUCTION

Copolymerization of carbon dioxide with epoxides in the presence of certain organozinc catalyst systems has been reported^{1,2} to yield alternating copolymers:



The polycarbonates so formed are linear³ and are of high molecular weight² ($[\eta] > 1$). They have been synthesized from a variety of epoxides including ethylene oxide, propylene oxide, epichlorohydrin, cyclohexene oxide, and styrene oxide.¹⁻⁶ Among the catalyst systems studied, diethylzinc in combination with water or a primary amine or a meta or para dihydric phenol appears to be particularly effective.^{3,5,6} Analysis of the copolymers by IR and NMR and their elemental composition show that the copolymers have alternating structures.²

In this communication, the transitions and thermomechanical spectra (~ 1 cps) of poly(ethylene carbonate), poly(propylene carbonate) and their 1:1 blend as determined by torsional braid analysis (TBA)⁷ are reported. The polymers are a recent development, and their thermomechanical properties (transitions) should be of considerable interest from the point of view of both theory and potential use.

EXPERIMENTAL

Samples of poly(ethylene carbonate) and poly(propylene carbonate) were obtained from Prof. Tsuruta's laboratories. The polymers were purified by reprecipitating three times from a chloroform solution into a large excess of rapidly stirred methanol. The precipitated polymers were then washed several times with methanol and dried overnight in vacuo at room temperature.

The NMR spectra of the polymers (dried further in vacuo at 50°C for 24 hr) in deuteriochloroform solution were recorded at 60°C using a Varian HA-100 spectrometer. Hexamethyldisiloxane was used as an internal reference.

Each specimen for torsional braid analysis was prepared by impregnating a glass braid in a 5% (w/v) solution of the polymer in chloroform and removing the solvent from the specimen in situ while mounted in the chamber of the instrument. Solvent was removed in the process of heating ($\Delta T/\Delta t = 3^\circ\text{C}/\text{min}$) the specimen to 120°C. A 1:1 blend (on the basis of the molecular weight of the repeat units) of the two homopolymers was obtained by using a homogenous mixture of their chloroform solutions.

Thermomechanical data were obtained throughout the temperature sequence of 120° → -190° → 120°C. All thermomechanical experiments were carried out in dried nitrogen. Details of the theory, technique, methods of data reduction, and conventions for presentation of data for torsional braid analysis have been published.⁷ Transitions are designated by the temperatures of the damping peaks.

RESULTS AND DISCUSSION

The 100-MHz NMR spectra of poly(ethylene carbonate) and poly(propylene carbonate) are shown in Figure 1. By comparison with the NMR spectra published earlier² and invoking the same arguments concerning spectral interpretation, it is apparent that the two homopolymers have essentially alternating structures.

The thermomechanical spectra of poly(ethylene carbonate) and poly(propylene carbonate) and their 1:1 blend are shown in Figures 2, 3, and 4. The transitions, T_g and T_β , the ratios of T_β °K/ T_g °K, and the intensities of the β -peaks for the homopolymers and their blend are summarized in Table I.

The presence only of a glass transition and a glassy state relaxation in the thermomechanical spectra indicates that poly(ethylene carbonate) and poly(propylene carbonate) are amorphous in nature. The sharp damping peaks and the drastic drop in their rigidities at 22°C (0.5 cps) for poly(ethylene carbonate) and at 41°C (0.4 cps) for poly(propylene carbonate) are associated with their glass transition temperatures; both polymers display a glassy-state β -transition at about -85°C. Relative to the intensity of the glass transition peak, the low-temperature loss peak of poly(ethylene carbonate) is more intense than that of poly(propylene carbonate). Furthermore, the β -peak of poly(ethylene carbonate) is about twice as intense as and more asymmetric than the β -peak for poly(propylene carbonate).

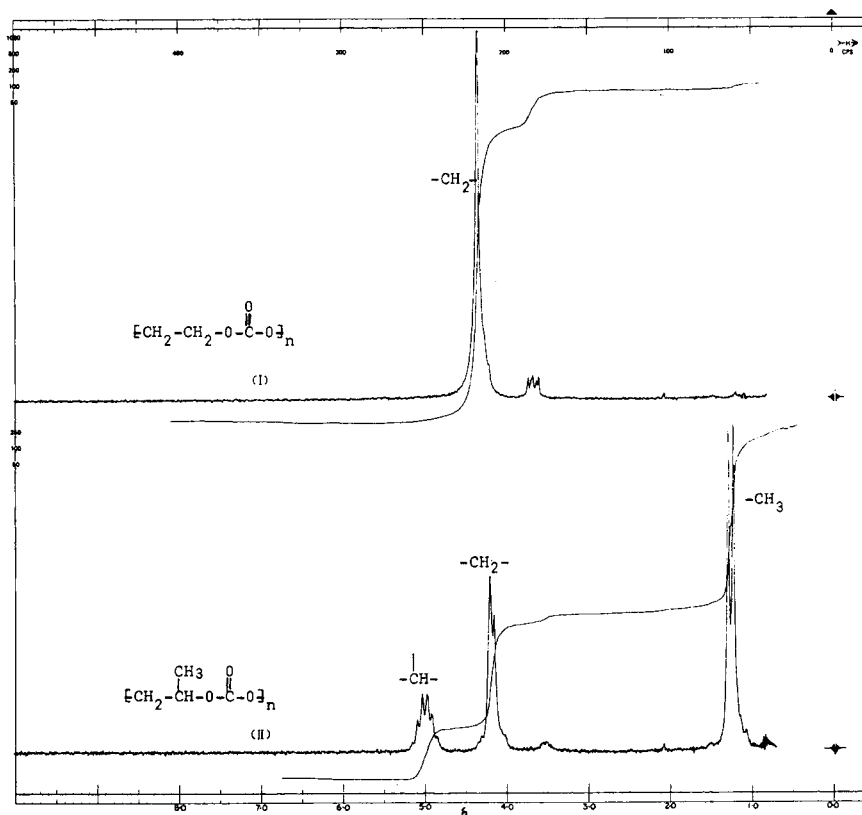


Fig. 1. 100-MHz NMR spectra of (I) poly(ethylene carbonate) and (II) poly(propylene carbonate).

TABLE I
Transitions of Poly(ethylene Carbonate),
Poly(propylene Carbonate), and their 1:1 Blend

Polymer	T_g , °C	T_β , °C	T_β , °K/ T_g , °K	Intensity of β -peak
Poly(ethylene carbonate)	22 (0.5 cps)	-83 (1.0 cps)	0.64	0.10
Poly(propylene carbonate)	41 (0.4 cps)	-85 (0.9 cps)	0.60	0.05
Poly(ethylene carbonate)/poly(propylene carbonate) (1:1)	26/40	-80 (1.0 cps)		0.08
Poly(bisphenol A carbonate)	150	-100	0.41	—

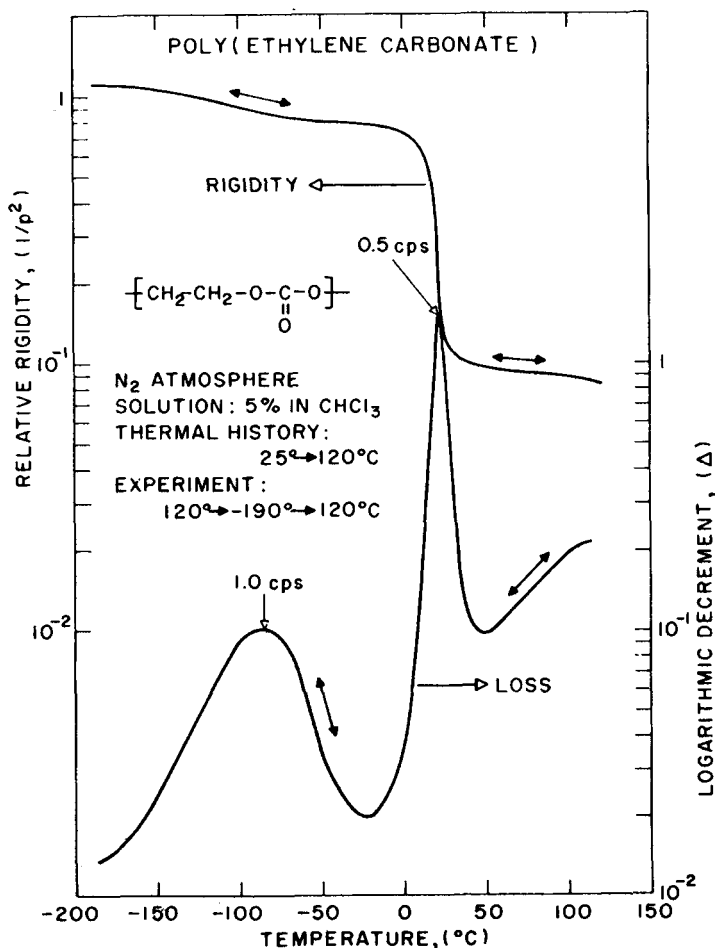


Fig. 2. Thermomechanical spectrum of poly(ethylene carbonate).

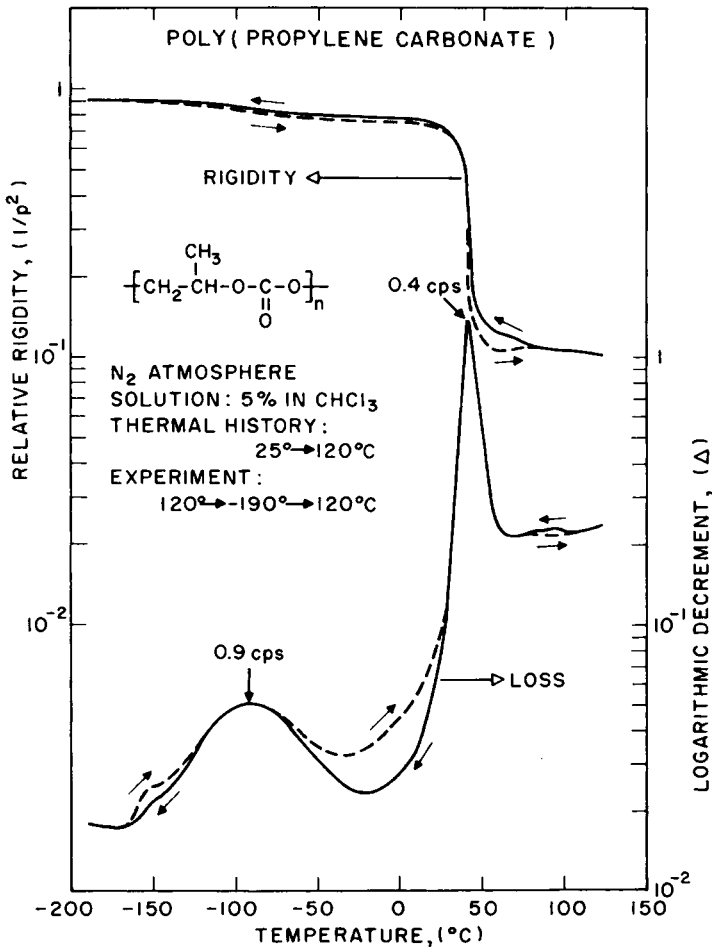


Fig. 3. Thermomechanical spectrum of poly(propylene carbonate).

On the basis of intramolecular geometrical factors, the T_g of the poly(ethylene carbonate) would be expected to be lower than that of poly(propylene carbonate), which is indeed the case. The rigidity and polarity of the carbonate linkage in affecting localized motions is revealed by comparison of the T_g of poly(propylene carbonate) (41°C, 0.4 cps) with that of partially crystalline poly(propylene oxide) (-62°C, 0.6 cps).^{8,9}

In consequence of absence of side groups, the β -peaks must be associated with in-chain motion of short segments of polymer chains. The decreased intensity of the β -peak in poly(propylene carbonate) is presumably a result of the increased bulk factor of the methyl group in restricting motion. Although the carbonate linkage is involved in the β -process of amorphous poly(bisphenol A carbonate) ($T_\beta = -100^\circ\text{C}$)¹⁰, the present aliphatic polymers have additional low-energy modes for motion in the hydrocarbon linkages. These appear to be more than counterbalanced by increased intermolecular factors which thereby raise the temperature of their β -peaks relative to that of the aromatic polycarbonate. It is interesting to note that the T_β °K/ T_g °K ratios of these aliphatic polycarbonates (~ 0.6) are closer to the values usually experienced by linear polymers (~ 0.7) than that of the aromatic polycarbonate (~ 0.4).

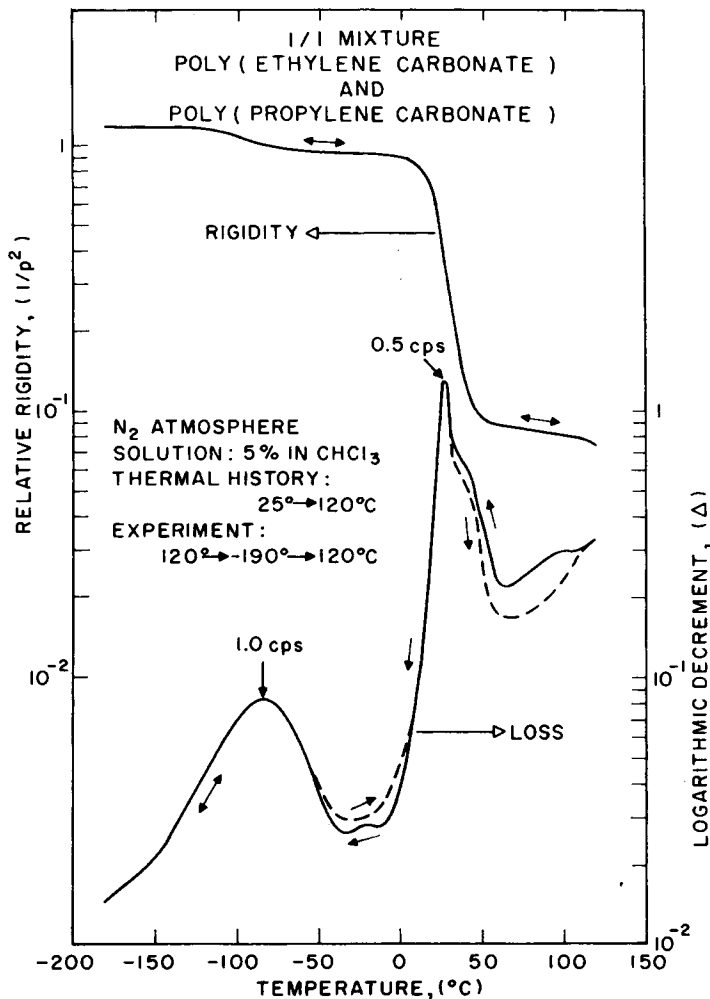


Fig. 4. Thermomechanical spectrum of a 1:1 blend of poly(ethylene carbonate) and poly(propylene carbonate).

Poly(propylene carbonate) displays much more thermohysteresis than poly(ethylene carbonate) both in rigidity and damping between the cooling and subsequent heating experiments. Formation of microcracks (on cooling) in the embrittled polymer specimen could lead to a decreased rigidity and increased damping on subsequent heating. The observed thermohysteresis in the case of poly(propylene carbonate) could be the consequence of the methyl groups on the polymer chain which presumably weaken intermolecular cohesive forces. Such behavior has been noticed in polymers such as poly(2-methyl-1-butene),¹¹ poly(*t*-butyl methacrylate),¹² poly(methyl methacrylate),¹³ and polystyrene.¹³ Based on a study of a correlation between brittle fracture and molecular cross-sectional area of polymers, it has been argued¹⁴ that systematic variation in the critical tensile breaking stress of polymers is a consequence of variations in the distance between adjacent molecules caused by bulky side groups and other steric factors.

In the case of a 1:1 blend of poly(ethylene carbonate) and poly(propylene carbonate), the presence of a damping peak (at 26°C) and a shoulder (around 40°C) suggests that

the blend is a two-phase mixture and not a homogeneous one-phase solution. The intensity of the β -peak is about midway between the intensities of the β -peaks of the individual constituents.

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