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### *Halato-Telechelic Polymers. IX. Some Specific Properties of Dicarboxylato Polymers Based on Group IVb Metal Ions*

Halato-telechelic polymers (HTP) result from the complete ionization of both ends of telechelic prepolymers. The behavior of a series of divalent cation- $\alpha,\omega$ -carboxylato polymers has been studied as well in solution as in bulk (1-5). In dilute solution, a sharp increase of viscosity can be observed at increasing concentrations, resulting in an early gelation (ca. 1 g/dL) in nonpolar solvents (1,4). The electrostatic origin of this type of behavior has been clearly established from the effect of a range of parameters, such as the nature of the ion pair, polarity of the medium, and temperature. The dilute solution properties of HTP in media of low dielectric constant is the consequence of an ion aggregation process and more specifically of ionic multiplets formation. At high concentrations, and accordingly in bulk, the ionic multiplets can possibly aggregate into clusters and, in some favorable conditions, into at least locally organized lamellar structures (3).

Because of the depressive effect of any polar compound on the ionic aggregation in mono- and divalent cation- $\alpha,\omega$ -carboxylato polymers, drastic conditions are required for the synthesis of representative and reproducible materials (4). Highly reactive metal alkoxides must be added in stoichiometric quantities and under an inert atmosphere into a carefully dried solution of the carboxy telechelic prepolymer. Finally, the alcohol formed in the reaction has to be completely removed from the reaction medium by azeotropic solvent distillation.

The sensitivity of carboxylato telechelic polymers based on mono- and divalent cations to polar agents is of course a drawback for easy characterization, handling, and applications. The less pronounced the ionic character of the metal carboxylate the less critical this situation is expected to be. In that prospect, we have been interested in the neutralization of carboxy telechelic polymers by transition metals of group IVb (Ti, Zr, etc.). Indeed Ti IV compounds are generally covalent in nature (6), whereas the entire behavior of Zr points to its non-ionic character in its compounds (7). This note reports the first results observed along these lines.

Added with a stoichiometric amount of magnesium methoxide, a carefully dried 5% solution of a carboxy telechelic polybutadiene (HYCAR CTB 2000 x 156 commercialized by B.F. Goodrich,  $\bar{M}_n = 4600$ ) gelatinizes as soon as the methanol formed is removed from the reaction medium. When tetra-n-butoxy-titanium  $[\text{Ti}(\text{On.Bu})_4]$  is substituted for magnesium methoxide, all the other experimental conditions being kept constant, only an increase in viscosity is observed, but no gelation. That means that the reaction of the carboxylic acid end groups with the stoichiometric amount of alkoxide groups (two carboxy telechelic polymers per Ti) occurs in such a way that the resulting product is not really crosslinked as expected. High steric hindrance could perhaps explain that the four n-butoxy groups of the titanium alkoxide are unable to react completely with a polymeric reagent. For instance, we have reported elsewhere that the

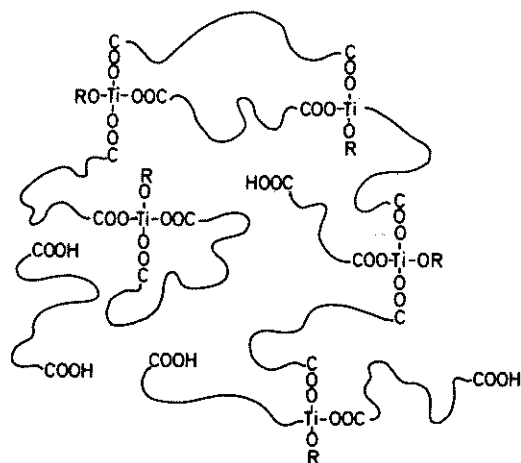


Fig. 1. Schematic description of the polymeric material resulting from the addition of tetra-*n*-butoxytitanium to carboxy telechelic polybutadiene ( $-\text{On.Bu}/-\text{COOH} = 1$ ).

replacement of the alkoxy groups of bimetallic oxoalkoxides  $[(\text{RO})_2\text{Al}-\text{O}-\text{Zn}-\text{O}-\text{Al}(\text{OR})_2]$  by a hydroxyl-terminated polystyrene ( $\bar{M}_n = 6000$ ;  $f_{\text{OH}} = 1.03$ ) was limited to 72% (8). To explain the absence of gelation at the addition of  $\text{Ti}(\text{On.Bu})_4$  to the stoichiometric amount of carboxy telechelic polybutadiene, it must be assumed that at least half the alkoxy groups of  $\text{Ti}(\text{On.Bu})_4$  remain unreacted which is quite questionable. It seems more realistic to suggest that more than 50% of the alkoxy groups of  $\text{Ti}(\text{On.Bu})_4$  react with the carboxylic acid end groups, but that, in dilute solution, the occurrence of intramolecular reactions favors a limited chain extension process, as tentatively represented on Figure 1. Furthermore, steric hindrance of the carboxylato alkoxy titanium units might also explain why ion-pairs association is not able to promote here the same gelation process as the one observed with mono- and divalent metals.

To avoid these drawbacks, an attractive approach is the addition of a sufficient excess of titanium alkoxide for capping as many chain ends as possible with a carboxylato alkoxy titanium; in a second step, the nonsubstituted alkoxy groups ( $\text{Ti}-\text{On.Bu}$ ) carried on the prepolymer chains will be hydrolyzed progressively to promote the formation of  $\text{Ti}-\text{O}-\text{Ti}$  intermolecular bridges, and accordingly of a crosslinked material. Indeed, the partial hydrolysis of the excess titanium alkoxide gives rise to  $\text{Ti}-\text{OH}$  groups which easily react with the not yet hydrolyzed  $\text{Ti}-\text{On.Bu}$  with formation of these  $\text{Ti}-\text{O}-\text{Ti}$  groupings and *n*-BuOH alcohol. According to the above-proposed reaction scheme, a previously dried solution of carboxy telechelic polybutadiene (Hycar CTB,  $\bar{M}_n = 4600$ ) in toluene (5 wt %) is added with a fivefold excess of *n*-butoxy titanium (i.e., 2.5 Ti per polybutadiene chain). Upon contact with atmosphere, the viscosity of the resulting solution increases steadily (Fig. 2), as measured by means of the Rotavisko

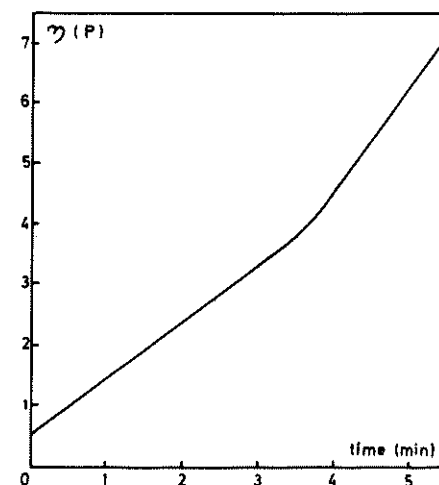


Fig. 2. Time evolution of the viscosity of 5-g/dL Ti carboxylato- $\alpha,\omega$ -polybutadiene solution in toluene. Just after addition of tetra-*n*-butoxytitanium ( $\text{Ti}/\text{COOH} = 1.25$ ) to the previously dried solution of the carboxy telechelic polybutadiene ( $\bar{M}_n = 4600$ ), the viscosity is measured in air at a shear rate of  $1 \text{ s}^{-1}$ .

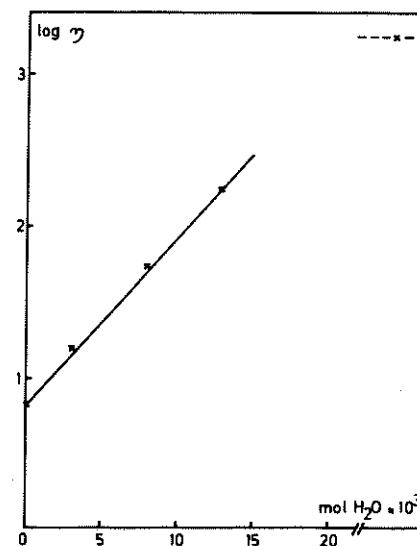


Fig. 3. Effect of addition of water on the viscosity of 5-g/dL Ti carboxylato- $\alpha,\omega$ -polybutadiene solution in toluene. ( $\text{Ti}/\text{COOH} = 1.25$ ). The viscosity ( $\eta$ ) is measured at a shear rate of  $1 \text{ s}^{-1}$ . The abscissa refers to the amount of water added to 50 mL of solution.

Haake rheometer operating at a  $1\text{-s}^{-1}$  shear rate. Furthermore, the viscosity increase is largely enhanced by addition of increasing amounts of water into the

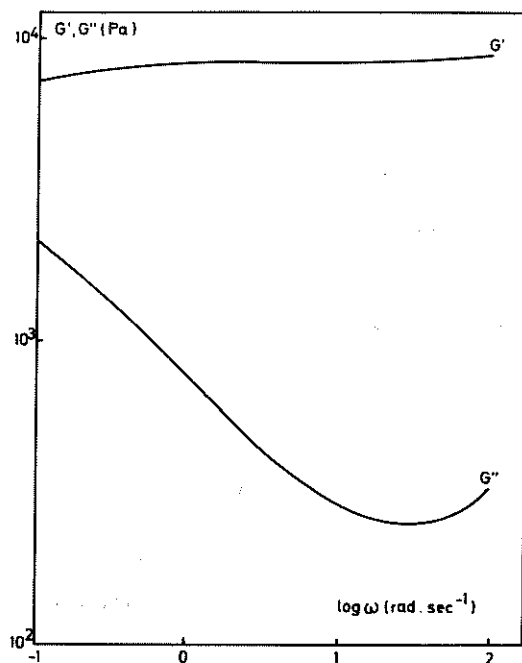


Fig. 4. Shear storage ( $G'$ ) and loss ( $G''$ ) moduli versus angular frequency at 296 K for 5-g/dL solution of Ti carboxylato- $\alpha,\omega$ -polybutadiene in toluene ( $\text{Ti}/\text{COOH} = 1.25$ ). The solution was previously added with water up to constant viscosity.

solution (Fig. 3). Finally, a constant viscosity (1800 poise) is reached and the solution exhibits all the characteristics of a gel. For instance, the dynamic viscoelastic behavior is characterized by a storage modulus ( $G'$ ) independent of the frequency and largely higher than the loss modulus ( $G''$ ) (Fig. 4). The dynamic mechanical properties of the solution have been investigated by means of the Rheometrics mechanical spectrometer RMS-7,200. For titanium, zirconium, and cerium cations, the gelation can be observed at polybutadiene concentrations lower than 1.5 g/dL.

In conclusion, in contrast with alcoholates of groups I and II, those of group IVb afford the important advantage of enabling the preparation of metal- $\alpha,\omega$ -carboxylato polymers stable at the contact of atmospheric moisture; better yet, the intervention of humidity is strictly necessary to form an efficiently cross-linked material. It is worthwhile to note that gelation is observed even though the alcohol formed by the neutralization reaction is not removed from the reaction medium. These results agree with the less pronounced ionic character of the metal (IVb) carboxylato bonds and with their low sensitivity to polar compounds.

Metals belonging to group IIIa exhibit a behavior quite similar to that of the metals of groups I and II, when their alkoxide is used in stoichiometric amounts

under anhydrous conditions; the corresponding carboxylato telechelic polymers, however, display a very satisfying stability in nonanhydrous environment. These metals can therefore also be used in the same experimental conditions as those described here for metals of group IVa.

The solution and bulk properties of metal (IVa)- $\alpha,\omega$ -carboxylato polymers by now are thoroughly studied to establish unambiguously their deformation mechanism, and the role played by the cation size on the network formation and its structure and stability. These results will be compared with those already reported (1-5) or to be published (as Parts VI, VII, and VIII of this series) for metal (I,II)- $\alpha,\omega$ -carboxylato counterparts. As the extent of the electrostatic and steric effects is expected to be largely different in these two types of carboxylato telechelic polymers, significant differences in their general behavior should also be expected.

#### Acknowledgments

The authors are very much indebted to both UNIBRA (Brussels) and the "Services de la Programmation de la Politique Scientifique" (Brussels) for support and fellowship (to G.B.). They are also grateful to Professor C. Marco (University of Mons, Belgium) for his collaboration in the rheological study of these materials, and to G. Renders for skillful technical assistance.

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Received November 20, 1981

Accepted March 1, 1982

Corrected proof received January 19, 1983