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Halato-telechelic Polymers

2. Glass Transition and Viscoelastic Behavior

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Summary

Halato-telechelic polymers (HTP) resulting from the neutralization of carboxy telechelic polymers behave as useful ion-containing model compounds. Carboxy telechelic polybutadiene ($\overline{Mn}$: 4,600) neutralized by magnesium methoxide exhibits a secondary relaxation mechanism characteristic of the ionic component. The activation process of this secondary relaxation obeys to an Arrhenius-type dependence and an activation energy of 30.5 Kcal/mole is calculated.

During the last fifteen years, the morphology and bulk properties of ion-containing polymers have been the subject of a rapidly growing interest (EISENBERG 1974 and 1977, HOLIDAY 1975). In particular, extensive studies have been devoted to ionomers, which are mainly non polar polymers carrying ionizable pendant groups distributed more or less randomly along the chain. In the bulk polymers these ionic groups aggregate in multiplets and clusters and exert then dominant influence on the properties of the material. A better insight on the fundamental structure-properties relationships for such products could be obtained from the study of model ionic macromolecules, i.e. halato-telechelic polymers (HTP) (BROZE 1980). These compounds result from the neutralization of carboxy telechelic polymers : e.g. for divalent cations.

$$n\ \mathrm{HOOC{-}P_x{-}COOH} + n\ \mathrm{Me^{++}X_2^{=}} \rightarrow \left[{}^{-}\mathrm{OOC{-}P_x{-}COO^{-}Me^{++}}\right]_n + 2\ n\mathrm{HX}$$

HTP are indeed interesting model compounds, thanks to the broad range of systematic modifications which can be applied to the nature, the mean length, and the

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polydispersity of P_x, as well as to the nature of the ionic groups. OTOCKA et al. (1969) and PINERI et al. (1974) have already considered such materials. The former were interested in the viscosity-molecular weight relationship whereas the latter investigated a possible supermolecular structure by SAXS. We have already discussed the gelation of HTP in the non-polar solvents (BROZE et al. 1981); the present note aims to report briefly the first results obtained in the investigation of polybutadiene (PBD)-based HTP by calorimetric, isochronal stress relaxation, and dynamic mechanical methods.

Carboxy-telechelic polybutadiene ($\overline{Mn}$: 4,600 and $\overline{Mw}/\overline{Mn}$: 1.8), commercialized by B.F. Goodrich under the trade name HYCAR CTB 2000x156, was neutralized in dry toluene by adding a stoichiometric amount of magnesium methoxide. Complete reaction was ensured by distilling off the methanol formed (BROZE 1980). After elimination of toluene the Mg-α,ω-dicarboxylato PBD (PBD-Mg) was dried under vacuum to constant weight.

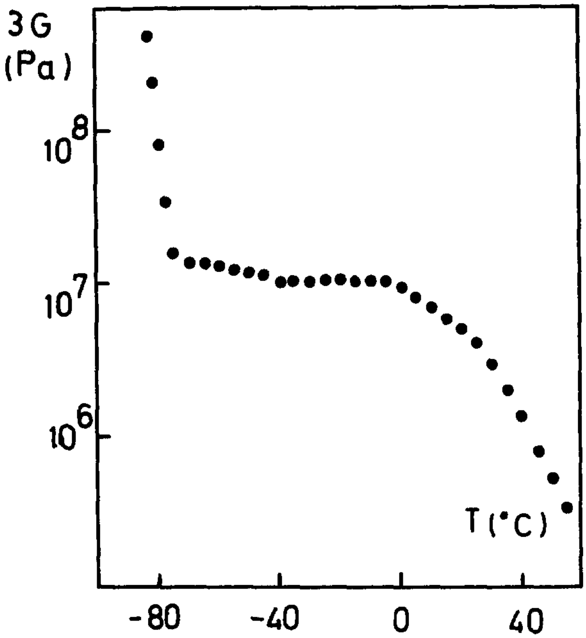

Figure 1 : Plot of 10-sec. torsion modulus versus temperature, for magnesium-α,ω-dicarboxylato-PBD (ion content : 2 mole %).

Differential scanning calorimetry (Du Pont - Thermal Analyzer - 990) shows the absence of any effect of the neutralization on the glass transition temperature Tg of PBD blocks (193°K). This behavior contrasts markedly with ionomers, the Tg of which depends significantly on the content of randomly placed ions (EISENBERG 1977).

The 10 sec. torsion modulus (Gehman pendulum) of PBD-Mg in the rubberlike plateau is rather high, and practically constant up to 273°K(Fig.1).As it is impossible to prepare self-consistent testing specimen, the non neutralized carboxy-telechelic PBD cannot be similarly characterized. This behavior confirms that Mg carboxylates act efficiently as chain extenders, and induce some degree of crosslinking and/or chain entanglements at least below 273°K.
Although there is a decrease in modulus starting around 273°K, a net characteristic flow behavior is observed above room temperature (RT). It is to be noted however that PBD-Mg at RT shows a SAXS peak which is interpreted as resulting from a regular aggregation of ionic groups; these results will be discussed elsewhere (BROZE et al.)

The dynamic mechanical behavior of PBD-Mg has been investigated by means of a Rheometrics Mechanical Spectrometer RMS-7200. The storage (G') and loss (G") moduli versus frequency isotherms have been recorded between 302 and 370°K. Time-temperature equivalence is verified for both G' and G" and Fig.2 shows the resulting mastercurves at 302°K. Since a maximum in G" values is not observed for the non neutralized PBD (Fig.3), that inflexion is accordingly attributed to a secondary relaxation mechanism characteristic of the ionic component. The shift factors (a_T) do not fit the WLF equation; no linear relation is observed by plotting (To-T)/log a_T againt (T-To) (with To : 302°K). The activation process of the secondary relaxation mechanism does not accordingly obey to the free volume theory. On the other hand, Fig.4 shows that the shift factors fit very well an Arrhenius-type of temperature dependence. From the slope of Fig.4, an activation energy of 30.5 K.cal/mole is calculated for a PBD-Mg with an ion content of 2 mole %.

The dynamic mechanical behavior of PBD-Mg is to be compared with results reported by EISENBERG (1977 and 1980) for styrene (S) - and ethyl acrylate (EA) - based ionomers. Thermorheological complexity was observed from and above ca. 6 mole % and 12-16 mole % of ions in S and EA ionomers respectively (failure of time-temperature superposition). This behavior was attributed to the occurrence of a secondary relaxation mechanism. By separating the simultaneous primary and

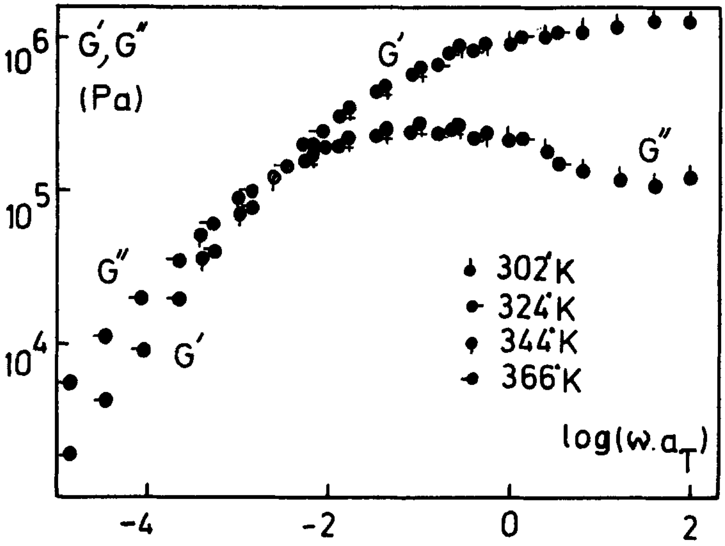

Figure 2 : Master curve of G' and G" versus reduced frequency, for magnesium-α,ω-dicarboxylato-PBD. Reference temperature 302°K. For clarity, only half the experimental points of 4 isotherms have been plotted on the figure. Furthermore isotherms measured at 313,334 and 354°K confirm the meaning of the time-temperature equivalence.

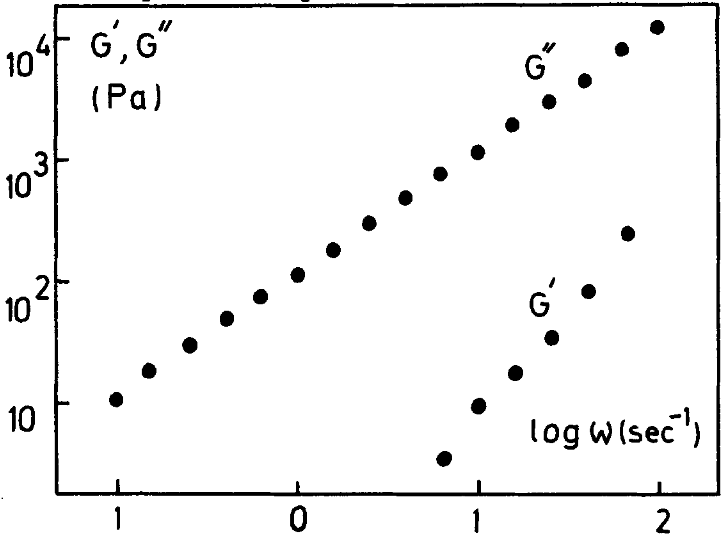

Figure 3 : Dynamic storage and loss moduli of carboxytelechelic polybutadiene ($\overline{Mn}$: 4,600) as a function of angular frequency at 302°K.

secondary relaxation, Eisenberg estimated for the latter an activation energy of 32 Kcal/mole for S ionomer (ion content of 7,7 mole %), and 10 to 17 Kcal/mole for the EA system. The onset of the thermorheological complexity was also seen to be qualitatively related to the size and charge of the cation. Except for the very low ion contents, the dependence of the shift factors on temperature defined two regions : the higher-temperature region corresponding to the flow process with an Arrhenius-type of temperature dependence, and the lower-temperature one (which includes Tg) for which it was difficult to decide if a WLF or an Arrhenius-type of equation was more adequate.

By contrast with S and EA ionomers, PBD-based HTP show an apparent independence of Tg on the ionic component, and an interesting thermorheological simplicity. In other words, the PBD-based HTP behave really as useful model compounds, since their secondary relaxation appears quite independently of the primary one, and can accordingly be studied without ambiguity. Furthermore, the secondary relaxation is already observed at rather low ion contents (ca. 2 mole %), and can be attributed to the ionic component itself.

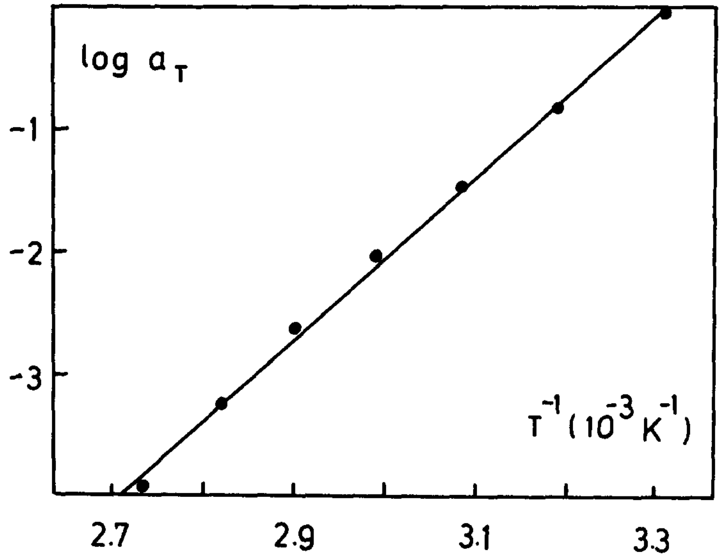

Figure 4 : Shift factors (a_T) versus 1/T, for magnesium-α,ω-dicarboxylato-PBD (ion content : 2 mole %)

The influence of both the ion content (regulated via prepolymer P_x molecular weight) and the cation characteristics (size, charge) on the secondary relaxation mechanism is now under study for polydiene-based HTP. A more complete account of this work will be published in the near future.

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