CHAPTER IV

CONCLUSIONS

4.1 The Master Curve

The viscoelastic properties of PMMA of two molecular weights, SAN and their blends were investigated. For all our polymers, viscoelastic functions measured at fixed temperatures can be superimposed onto a single master curve by using the time-temperature superposition principle. $G'(\omega)$ and $\tan\delta(\omega)$ master curves were generated continuously across the glass transition temperature. The master curves exibit three zones: the terminal zone, the entanglement plateau zone, and the transition zone. The existence of the entanglement plateau zone is consistent with other published results using polymers of high molecular weights.

4.1.1 Effect of Molecular Weight

In the rubbery zone or the entanglement plateau region, the master curve collapses partially. The width of the plateau region for higher molecular weights is wider than for lower molecular weight. This rubbery plateau region appears only when the molecular weight exceeds a critical molecular weight (M_c); our result is consistent with this well known fact. The plateau moduli (G_N^O) of the two PMMA's of different molecular weights are nearly the same, having a value about 1.4×10^6 dynes/cm^2. The plateau modulus G_N^O is therefore molecular weight independent, consistent with the reptation theory of Doi and Edwards. In the transition zone, $G'(\omega)$ of all our samples have the same $\omega^{1/2}$ dependence. The onset of the transition zone occurs at a frequency which

appears to depend on molecular weight. The inability to find a collapse of the master curves for the same polymer but at different molecular weights in the transition zone is attributed to a difference in M_e for our two samples which may have been caused by poor sample preparation. Theoretically, both M_c and M_e are expected to be structure/chemical and molecular weight independent. Another reason can be given in the framework of molecular weight distribution. The difference in molecular weight distribution of a given polymer type allows local couplings between chains of different lengths. Therefore, a cooperative effect and/or a complexity of the system can induce a variation of the onset for the transition regime.

4.1.2 Effect of Blending

The $G'(\omega)$ master curve of PMMA/SAN : 30/70 blend has three zones: the terminal zone, the entanglement zone, and the transition zone, similar to the master curves of pure components. The blend master curve is bound from above by the PMMA master curve and from below by the SAN master curve; an exception occurs in the entanglement zone where the blend master curve falls below that of SAN. It is possible that the exothermic interaction between PMMA and SAN is different from that of PS and acrylonitrile, inducing a larger M_e and a lower G_N^O.

4.2 The Shift Factor

The empirical shift factors above and below T_g show different temperature dependences. The empirical shift factors below T_g $(a_T)_\alpha$ show a stronger temperature dependence than those above T_g $(a_T)_\eta$. The WLF empirical equation can fit data quite well as long as the temperature is above T_g or in the

terminal zone (η-relaxation). The constants C_1° and C_2° are negative contrary to typical positive values often found in literatures because we have used a reference temperature well above T_g. At temperatures below T_g the temperature dependence of (a_T) does not follow the WLF equation.

The coupling model of relaxation is therefore applied to connect the different temperature dependences above and below T_g. This model dictates the relationship between the two corresponding shift factors above the T_g and below the T_g. The coupling parameters β_α below T_g and β_η above T_g obtained from the stress relaxation measurements are found to be different. β_η is greater than β_α for all samples because there are several molecular motions for the chains occuring in the terminal relaxation while there is only the local segmental motion of the chains occuring in the α relaxation. The coupling parameter β_η is less sensitive to polymer chemical structure whereas β_α depends strongly on polymer chemical structure. The relaxation times (τ^*) of both the segmental and terminal relaxations depend on polymer structure at a given temperature.

The shift factors $(a_T)_\alpha$ were calculated by the coupling model using β_α and β_η obtained from stress relaxation measurements whereas $(a_T)_\alpha$ were recalculated from the WLF equation. The calculations agree with the experimental shift factor $(a_T)_\alpha$ below T_g. Therefore, the coupling model of relaxation is successful in making a connection between the different temperature dependences of the $(a_T)_\alpha$ and $(a_T)_\alpha$ in the α and the η-relaxation processes.