SUMMARY

This PhD thesis deals with the study of the plasticization effect on the polymer glass transition in swollen poly(ethyl acrylate) polymer networks with non-polar solvents (1,4-dimethyl benzene, methyl benzene and ethyl benzene), the organization of solvent molecules within the polymer matrix and the respective molecular dynamics The study was focused on partially crystallized and amorphous polymer/solvent mixtures with varying the cross-linking degree in polymer matrix and the type of non-polar solvent.

The study of thermal transitions in these systems was carried out with Differential Scanning Calorimetry (DSC). The study of the molecular dynamics were performed with two dielectric techniques: Thermally Stimulated Depolarization Currents (TSDC) and Dielectric Relaxation Spectroscopy (DRS).

The experimental results have shown that the presence of solvent within the polymer matrix induces the same degree of plasticization regardless of the non-polar solvent type and the polymer cross-linking degree. In partially crystallized mixtures, the presence of non-crystalline phase is ascribed to kinetic reasons (entropic contribution) without invoking polymer-solvent interactions (enthalpic contributions). Moreover, polymer segmental motions were found to be activated in partially crystallized mixtures. Concerning the amorphous mixtures, the presence of dynamic heterogeneity is originated by the high mobility contrast between two components without meaning immiscibility. The high degree of swelling in polymer networks inhibits the cooperativity of the polymer segmental dynamics close to the glass transition temperature, whereas theoretical models (Lodge and McLeish) adjusted to polymer mixtures describe very well the experimental results.