

Use of Thermogravimetry in the Study of Polymer–Solvent Interactions near Glass Transition Temperature

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Glass transition temperature is an important characteristic parameter of polymers, and, for most of the polymer applications, it indicates the highest usable temperature. Generally, it is determined from the techniques based on thermally stimulated processes such as differential thermal analysis, differential scanning calorimetry, dilatometry, etc.¹ Mechanical and dielectric relaxation spectroscopy are also important tools in the diagnosis of various polymeric transitions including the glass transition.² This note presents some interesting results obtained from thermogravimetric (TG) experiments where we have been able to identify glass transition temperature (T_g) of some polystyrene (PS) polymers. Conventionally, TG experiments are performed to provide information concerning thermal decomposition, thermal stability, chemical reactions, and physical changes involving change in the mass of polymer.¹ The present study indicates that TG technique can be used in the study of polymer–solvent interactions also.

Polystyrene, polystyrene–chloranil complex (PS–CA), and poly(styrene–allyl alcohol) copolymer (PSA) were investigated. Films of the polymers were prepared by the solution casting technique. After evaporation of the solvent at room temperature, the films were dried in an air oven at 50°C for 24 h. For TG experiments, these films were cut into fine pieces to ensure good thermal contact with the sample holder. A Stanton Redcroft TG-750 thermobalance was used for recording TG thermograms in static air. The heating rate was kept at 10°C/min.

Figure 1(a) shows a TG thermogram of PS. The polymer is stable up to 220°C with no loss in weight. Above this temperature, there is a rapid loss in the weight of sample, and we denote this temperature as the initial degradation temperature (IDT). Interesting features in the thermogram are observed if the films are prepared in tetrahydrofuran (THF) instead of the usual solvent benzene. A small loss in the weight of sample has been observed at low temperature and later a rapid decrease as the temperature reaches IDT for PS films prepared in THF, as shown in Figure 1(b). The initial loss in the weight of sample suggests a transition, and its temperature is close to the T_g of PS (96°C) obtained by TSD technique.³ We performed TG experiments on films of PS–CA and PSA prepared in THF [Fig. 1(c) and 1(d)] and obtained similar results. The T_g of these two polymers have been found to be 77°C³ and 58°C,⁴ respectively. For all the three polymers,

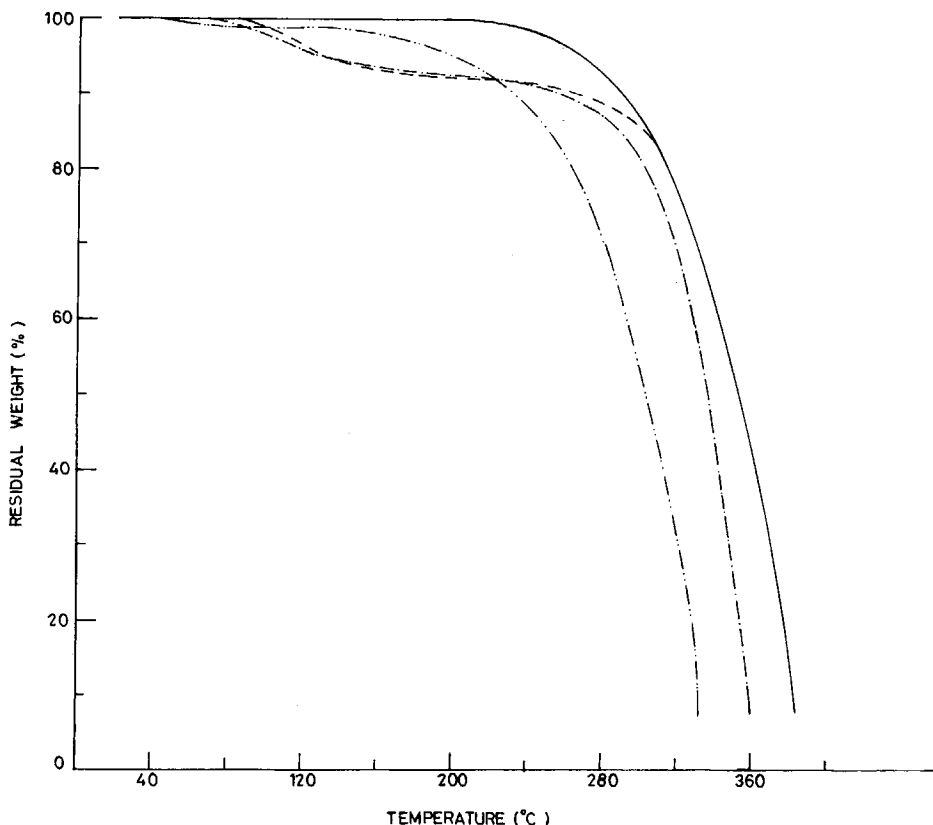


Fig. 1. TG thermograms of polystyrene polymers (films) in static air at a heating rate of 10°C/min: (a) (—) PS (cast from solution in benzene); (b) (- - -) PS(THF); (c) (- · - · -) PS-CA(THF); (d) (- · · · · -) PSA(THF).

no loss in the weight of sample was observed up to the onset of degradation when the films were prepared with benzene as a solvent.

It is quite likely that some kind of polymer-solvent interaction is taking place, on using THF as a solvent, that prevents its complete evaporation in the normal procedure of film preparation. The proposed molecular interaction possibly vanishes at T_g due to the onset of Brownian motion of the polymer chain segments at this temperature. This allows release of the THF molecules which evaporate, resulting in a decrease in the polymer mass as shown by the thermograms. Polymer-solvent interaction with THF as a solvent has been observed for styrene-acrylonitrile polymer also.⁵

The results of our experiments suggest the usefulness of simple thermogravimetry in the study of polymer-solvent interactions near T_g . This kind of investigation needs to be extended to other polymer systems also to establish a wider applicability of the TG technique in the proposed direction.

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