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INVESTIGATION OF THE SOLUTION CRYSTALLIZATION BEHAVIOUR OF POLYCARBONATE

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SUMMARY

On investigating bisphenol A polycarbonate (PC) samples in tetrahydrofuran by combined size-exclusion chromatography (SEC) and low-angle laser light scattering photometry, we found that elution behaviour depends on the preparation of the solution. Under certain conditions, microcrystallites are formed, passing the SEC columns with a very low elution volume, thus simulating a bimodal distribution of the molar masses of the polymer sample.

The formation of microcrystallites is caused by a solution-induced crystallization of the original amorphous material during the dissolution process.

PC crystals formed by solution-induced crystallization show a higher melting point than the melting point region for PC given in the literature. Compared to the original sample, the molar mass distribution function is shifted to higher values. The history of the solutions is important for the crystallization phenomena.

INTRODUCTION

Many properties of polymers depend on the molar mass (M) and, since synthetic polymers are always polydispersed with respect to M one important way to characterize a given polymer is to determine its molecular mass distribution (MD) by an appropriate method. Such a method has been established by combination of size-exclusion chromatography (SEC) with low-angle laser light scattering photometry (LALLS)^{1,2}. In an earlier paper, we reported on the apparatus as well as on the possibilities and some of the problems of this analytical tool³.

One prerequisite for making use of SEC-LALLS is the complete solubility of a given polymer sample in an eluent suitable for SEC columns. Since many polymers show limited solubilities, this requirement often leads to severe problems with currently used eluents. In the case of polycarbonate (PC), tetrahydrofuran (THF) is often used in SEC experiments, in spite of its only limited quality as a solvent for PC⁴. In fact, this system leads to problems in SEC-LALLS, which are discussed here along with procedures proposed to overcome these difficulties.

EXPERIMENTAL

The PC used in this study was Makrolon (Bayer, Leverkusen, F.R.G.), a granular material based on bisphenol A [poly(oxycarbonyloxy-1,4-phenylene-2,2-propylene-1,4-phenylene)]. Solvents of analytical quality were dried and freshly distilled, filtered through a 0.5- μm filter (Millipore, Waters Assoc., Eschborn, F.R.G.) and degassed by ultrasonic treatment. The experimental set-up and the equipment used for the SEC-LALLS measurements have been reported earlier³. Columns: $\mu\text{Porasil GPC } 60 \text{ \AA}$ (Waters Assoc., Milford, MA, U.S.A.) and LiChrospher Si 100 and Si 300 (Knauer, Bad Homburg, F.R.G.). Chromatographic parameters: temperature, 25°C; flow-rate, 1 ml/min; injection volume, 0.1–0.25 ml; sample concentration, $5 \cdot 10^{-3}$ g/ml.

RESULTS AND DISCUSSION

Fig. 1 shows an SEC curve of polycarbonate dissolved in THF at room temperature without stirring. The tracing of refractive index differences shows only one peak, whereas LALLS detects a second one in front of the main peak, indicating a high-molecular-mass fraction or aggregates. The second peak changes in size, depending on the conditions chosen for preparing the solution. Therefore, a more detailed investigation of the conditions of preparation seems to be needed.

We first noticed that the PC samples could not be dissolved completely in THF at room temperature without stirring. Normally, there was a residue of *ca.* 40% (w/w), which dissolved only on heating the mixture above 60°C. It is known from the literature that PC crystallizes from a melt or solution and that the crystalline material has a much lower solubility than its amorphous counterpart^{4–8}. The reason for this behaviour is not yet understood. Differential scanning calorimetry (DSC) measurements of the separated, insoluble portion of the PC samples showed a melting peak with a maximum value at 245°C, which is significantly higher than the melting range of 220–230°C reported in the literature⁴.

One possible explanation of the heading peak now seems to be the formation,

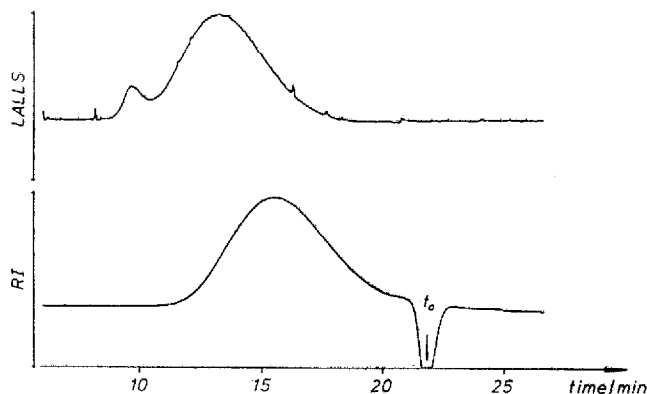


Fig. 1. Chromatogram of a PC sample in THF, showing the effect of an incomplete solution, possibly due to microcrystallites.

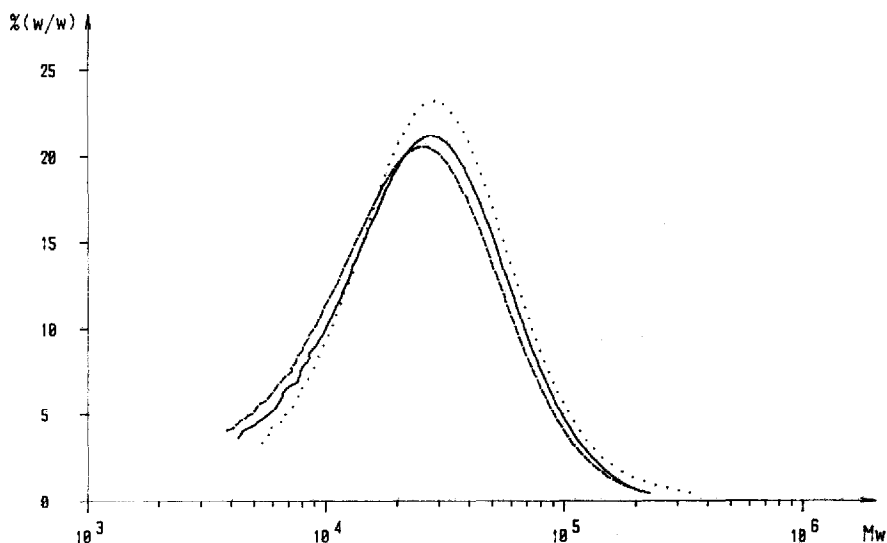


Fig. 2. Differential distribution functions of molar masses: ----- dissolved portion, $\bar{M}_w = 2.76 \cdot 10^4$ g/mol ($\bar{M}_w/\bar{M}_n = 1.89$); ——— original sample, $\bar{M}_w = 3.05 \cdot 10^4$ g/mol ($\bar{M}_w/\bar{M}_n = 2.06$); undissolved material, $\bar{M}_w = 3.27 \cdot 10^4$ g/mol ($\bar{M}_w/\bar{M}_n = 1.70$).

during the dissolution process, of microcrystallites consisting of several polymer molecules; with stirring, the granulate dissolves completely in most cases. A transformation from the amorphous to the crystalline state must occur in a swollen phase during the dissolution process.

One may imagine that the time a polymolecule remains in a high-concentration transition zone between solid and solution is decisive, whether or not a molecular orientation suitable for a crystalline arrangement (nucleus) is achieved. The lower the stirring rate, the higher the probability for such a nucleation process, and, as a result, the higher the probability for the formation of microcrystallites. Sometimes the microcrystallites are so small that they are not visually detectable and may pass through the column and, hence, simulate a bimodal distribution curve, as shown in Fig. 1.

The solution-induced crystallization is accompanied by a fractionation effect, as shown in Fig. 2. The distribution curve of the crystalline material is shifted to a higher M value, whereas that of the remaining soluble portion is shifted to a lower value, compared with the original sample. Both curves show less heterogeneity than that of the original sample. A corresponding behaviour was found for the system polyethylene xylene by Sadler⁹.

As the solution process is favoured by a high specific area of the solid material before the solution process, one may cast thin films from solutions of PC in a good solvent, *e.g.* dichloromethane, before dissolving it in THF. However, the conditions chosen for the formation of the films must be such as to prevent crystallization. Making films by evaporating the solvent at room temperature often leads to the formation of spherulitic crystals, which at temperatures below 60°C are insoluble in THF.

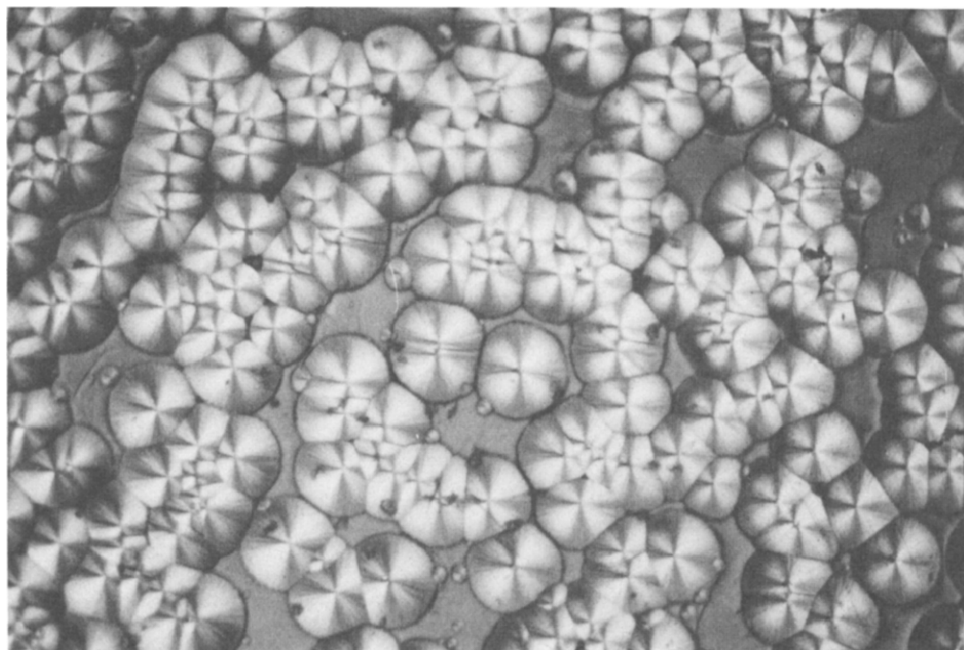


Fig. 3. PC spherulites found in a thin polymer film. The photomicrograph was taken with crossed polarizers. Magnification $50\times$.

The photomicrograph in Fig. 3 shows that even "transparent" films may contain crystalline material, since below a certain size the crystallites are not visually detectable.

CONCLUSION

A light-scattering device such as LALLS, as a complement to the common concentration-sensitive detector in SEC, is suitable for the evaluation of unexpected changes in polymer composition. Its sensitivity increases with increasing M . An analytical problem, which could only be observed by the use of a combination of SEC and LALLS, is explained by a solution-induced crystallization of PC in THF. The microcrystallites thus formed can pass through SEC columns but are undetectable by a differential refractive-index detector.

The solution-induced crystallization of PC and its fractionation effect on the original sample may be prevented by appropriate preparation of the solution, *e.g.* annealing at elevated temperatures.

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