(I) requires 86.1. The infra-red spectrum (*Figure 1*) showed an ester carbonyl peak at 1740 cm^{-1} and no features indicating hydroxyl or carboxyl. The mass spectrum included the following elements of most significance; m/c 344 [M$^+$] (54%): 301 (8%); 285 (6%); 217 (26%); 173 (97%); 113 (49%); 99 (82%); 86 (52%); 55 (100%); 41 (45%).

The glycol mother liquor, after removal of substance (I) from the autoclave distillate, was sampled and saponified quantitatively in 1% sodium hydroxide solution in 50% aqueous ethanol. After correction for a small titrateable acidity, the filtrate sample was found to have a saponification equivalent of 1044, corresponding to a residual content of 8.25 wt % of esters calculated as cyclic oligomer. However, the solubility of pure cyclic dimer (I) in glycol is only of the order

of 1%, suggesting that another substance was present in the mother liquor from (I).

After vacuum dehydration to still head temperature 54°C at 0.1 mm (water loss equal to 4.1% of sample weight), a sample of the filtrate (n_D^{25} 1.4315) was chromatographed on a column of silicone polymer OV–101 stationary phase on diatomite CLQ support at 200°C. Following the glycol peak was a major 'unknown' peak at a retention time of 1 min and a minor peak at 4.4 min, the apparent weight ratio of 'major' to 'minor' components being 10:1 approximately. The minor peak had the same retention time as samples of the purified cyclic dimer (I) added either in glycol or methanol solution. It was concluded that the major non-glycol component of the filtrate was an ester of vapour pressure rather lower than glycol but

considerably higher than that of cyclic dimer (compare with Carothers cyclic monomeric tetramethylene succinate, isomeric with ethylene adipate, b.p 95°–96°C/2 mmHg). Evidence that this may be the cyclic monomer (*MW* 172) was given by the mass spectrum obtained from the glycol filtrate with the main relevant features: m/c 172 [M+], 142, 129 112 and 99.

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Partial chain coupling of anionically prepared polymers by air termination

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It is well recognized that certain anionic polymerization systems can yield chains possessing near monodisperse molecular weight distributions. In the course of work carried out in these laboratories over the last few years, we have observed that the air termination of chains bearing the lithium counterion can induce the formation of a 'dimer' of the parent species. The formation of such a species is, of course, not observed when chain termination is accomplished by proton transfer. This Note presents a summary of our findings which apparently show that termination by the atmosphere can convert an initially near monodisperse molecular weight distribution into one exhibiting distinct bimodal character.

EXPERIMENTAL

The anionic polymerizations were carried out under high vacuum conditions using the experimental techniques described elsewhere[1]. The mono-

mers and solvents were purified by procedures outlined previously[1]. Purified sec-butyllithium was used as the initiator. Tetramethylethylenediamine (TMEDA) was purified by drying over calcium hydride and then exposure to dibutylmagnesium.

Gel permeation chromatography (g.p.c.) was used to examine the molecular weight distributions of homo and block copolymers prepared in this work. Tetrahydrofuran was the carrier solvent while the Waters differential refractometer was the detection instrument. Solvent flow rates of 1 and 0.25 ml/min were used.

Two different g.p.c. column arrangements were used in this work. These column sets were made up of 4 ft Styragel columns. The four column set had a porosity range of 5 × 10^3 to 7 × 10^5 Å while the five column set had a porosity range of 2 × 10^3 to 7 × 10^5 Å. Both column arrangements were such that no gaps in porosity existed within the range covered. Termination was accomplished by ex-

posure of the chain ends to degassed methanol or the atmosphere.

All of the chromatograms with the exception of *Figure 2*, curve B were run on the 5 column set. Chromatograms in *Figure 1* (curves A and B) were run at the 0.25 ml/min flow rate while the remaining chromatograms were run at the rate of 1 ml/min. The number-average molecular weights of the polymers prepared in this work ranged from 8 × 10^4 to 1.2 × 10^5 g/mol.

RESULTS AND DISCUSSION

Apart from the usual possible impurities, the common terminating components in the air are water vapour, carbon dioxide and oxygen. Carbon dioxide has been shown[2] to lead to chain coupling involving polystyryl lithium while oxygen is claimed[3] to cause the coupling of organolithium compounds when TMEDA is present. Recently, g.p.c. results have appeared which show[4,5] that the anionically prepared Dow S-102 and S-109 polystyrenes contain high molecular weight components which seem to be near monodisperse in molecular weight. Some of these species seem to have molecular weights double that of the parent polymers.
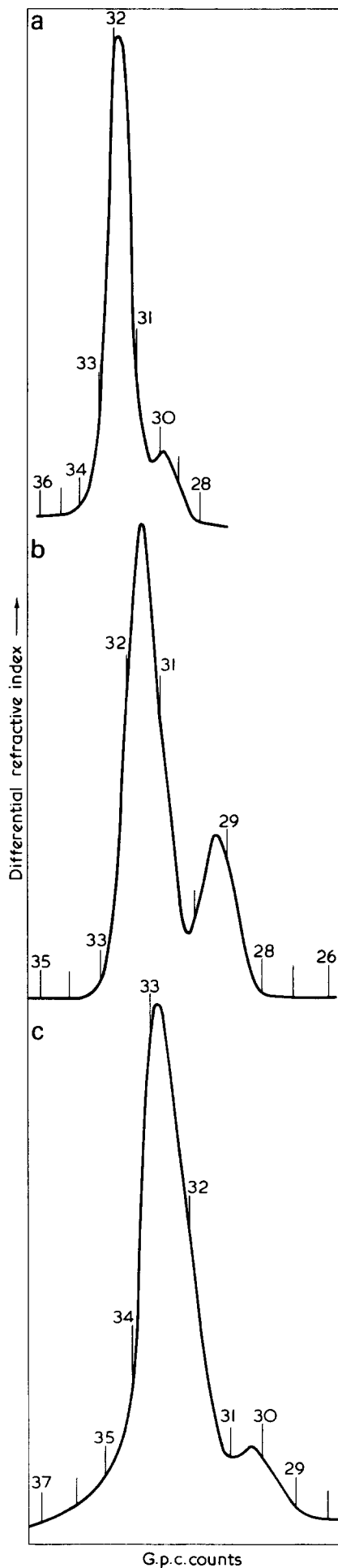
Figure 1 contains three chromatograms of block copolymers exhibiting bimodal molecular weight distributions. These three block copolymers were terminated by opening the reactor and allowing the active chain ends, poly (*p*-t-butylstyryl) lithium, polystyryl lithium or polybutadienyl lithium, in benzene, to react directly with the atmosphere. The shoulder in the forward portion of each chromatogram appears to be a narrow and symmetrical peak. This feature is reminiscent of what has been reported[4,5] for the Dow S-102 and Dow S-109 (the NBS 705)[4] polystyrenes. Chromatogram (B) of *Figure 1* indicates that air termination can yield as much as 20% or so coupled material. Thus, in this particular case a product was formed containing a significant amount of pentablock copolymer.

Recent work[3] has claimed that TMEDA will enhance the coupling of organolithium compounds when these species are exposed to oxygen. *Figure 2* contains two chromatograms of polybutadienes, one of which (*Figure 2a*) was terminated by methanol while the other (*Figure 2b*) was terminated by opening the reactor to the air. Both of these materials were prepared in a tetrahydrofuran—TMEDA (98/2% v/v) mixture at 0°C. While the chromatogram of the methanol terminated polybutadiene indicates a near monodisperse molecular weight distribution, the air terminated sample is bimodal and contains at least 40% coupled material. So far, it has been observed that polar solvents will apparently yield a greater fraction of coupled material upon air termination than will a corresponding system prepared in a hydrocarbon solvent. This is somewhat surprising since these active chain ends are associated in pairs in hydrocarbon solvents[6,7] but are completely unassociated in polar solvents[8]. Qualitatively, it might have been anticipated that the close proximity of the chain ends in hydrocarbon solvents could have led to a greater degree of chain coupling on exposure to air than is found for systems where no chain end chain association occurs.

It was noted[9] some time ago that the exposure of difunctional polystyryl sodium in tetrahydrofuran to oxygen

Figure 1 Chromatograms of air terminated block copolymers: (A) poly(*p*-t-butylstyrene-butadiene-*p*-t-butylstyrene); (B) poly (styrene—butadiene—styrene); (C) poly(*p*-t-butylstyrene—butadiene)
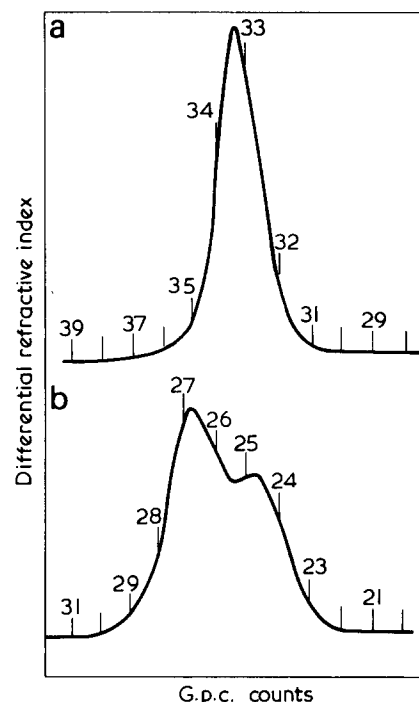

Figure 2 Chromatograms of polybutadiene: (A) terminated via methanol; (B) air terminated

led to an increase in solution viscosity. The suggested mechanism involved the formation of free radical chain ends followed by the coupling reaction. The results of our work do not allow us to determine the exact coupling mechanism (or mechanisms). However, the representative chromatograms shown in *Figures 1* and *2* do reveal that air termination of these anionic polymerizations can seriously distort what is initially a near monodisperse molecular weight distribution. Hence, although experimentally easy, air termination of anionic polymerizations involving the lithium counterion should be avoided if the molecular weight distribution is to remain unperturbed.

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