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Liquid Tin(II) Alkoxide Initiators for Use in the Ring-Opening Polymerisation of Cyclic Ester Monomers

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Abstract : The main aim of this research has been to design and synthesize some completely soluble liquid tin(II) alkoxide initiators for use in the ring-opening polymerisation (ROP) of cyclic ester monomers. This is in contrast to conventional tin(II) alkoxides in solid form which tend to be molecular aggregates and difficult to dissolve. The liquid initiators prepared were bis(tin(II) monooctoate) diethylene glycol ([Sn(Oct)]2DEG) and bis(tin(II) monooctoate) ethylene glycol ([Sn(Oct)]2EG). Their efficiencies as initiators in the bulk ROP of ε-caprolactone (CL) at 130oC were studied kinetically by dilatometry. Kinetic data over the 20-70% conversion range was used to construct both first-order and zero-order rate plots. It was found that the rate data fitted more closely to first-order kinetics with respect to the monomer concentration and gave higher first-order rate constants than the corresponding tin(II) octoate/diol initiating systems normally used to generate the tin(II) alkoxide in situ. Since the ultimate objective of this work is to produce copolymers suitable for biomedical use as absorbable monofilament surgical sutures, poly(L-lactide-co-ε-caprolactone) 75:25 mol %, P(LL-co-CL), copolymers were synthesized using both solid and liquid tin(II) alkoxide initiators at 130°C for 48 hrs. The statistical copolymers were obtained in near-quantitative yields with compositions (from 1H-NMR) close to the initial comonomer feed ratios. The monomer sequencing (from 13C-NMR) was partly random and partly blocky (gradient-type) due to the much differing monomer reactivity ratios (rLL >> rCL). From GPC, the copolymers obtained using the soluble liquid tin(II) alkoxides were found to have higher molecular weights (Mn = 40,000-100,000) than those from the only partially soluble solid initiators (Mn = 30,000-52,000).

Keywords : biodegradable polyesters, poly(L-lactide-co-ε-caprolactone), ring-opening polymerisation, tin(II) alkoxide
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