Letters

Stereospecific poly(isobutyl vinyl ether): use of phosphoryl chloride, thionyl chloride and vanadium pentoxide as catalysts

Introduction

In earlier publications[1–3] we reported that phosphoryl chloride and thionyl chloride initiate the cationic polymerization of α-methylstyrene and *N*-vinylcarbazole. Vinyl ethers become charred in presence of these initiators at all workable concentration ranges, but we now report that both $POCl_3$ and $SOCl_2$ can not only initiate the polymerization of isobutyl vinyl ether (IBVE) when used in combination with aluminium triethyl, but can also, under certain conditions, impart stereoregularity. In this context, we further report the formation of stereospecific poly(IBVE) by using a V_2O_5–$AlEt_3$ catalyst system, V_2O_5 alone being known to initiate the cationic polymerization of IBVE[4], and also of *N*-vinylcarbazole[5,6].

Experimental

IBVE, solvents and initiators were purified by standard methods. $AlEt_3$ was used in benzene solution. All polymerizations and necessary dilutions were carried out under nitrogen. The polymers were precipitated with ammoniacal methanol at the end of the desired time, purified by washing with methanol, HCl and water and finally dried in vacuum (1.5 mm) at 60°C.

As a measure of stereospecificity we used the value of index of stereospecificity defined by Hirata and Tani[7] as the percentage of the weight of MEK insoluble fraction against the total polymer yield. Fractionation of the polymer was carried out by following the procedure of Hirata and Tani[7].

Results and Discussion

All relevant results are summarized in *Table 1*. It may be observed that $AlEt_3$ alone fails to polymerize IBVE which is consistent with the observations of other workers[8]. The polymerizations occur in a homogeneous phase, and are sufficiently slow in presence of $AlEt_3$. However, without $AlEt_3$, IBVE has been observed to undergo rapid polymerization in presence of V_2O_5 [4], and charring in presence of $POCl_3$ or $SOCl_2$. *Table 1* also suggests that the conversion decreases and the index of stereospecificity increases with increasing $[AlEt_3]/[\text{initiator}]$ ratio. Another pertinent feature of these catalyst systems is their ability to impart stereoregularity at ambient temperature. Aging procedure also appears to have a significant effect. Thus, if the monomer and $AlEt_3$ are aged first, followed by the addition of the initiator, conversion decreases but stereoregularity is favoured (*Table 1*). On the other hand, converson increases and stereoregularity is suppressed when the initiator and $AlEt_3$ are aged first, followed by the addition of IBVE.

The effect of some organic halogen compounds such as t-butyl chloride on the polymerization of IBVE in presence of $AlEt_3$ was also examined. t-Butyl chloride alone can initiate IBVE polymerization in benzene as medium sufficiently fast. However, the rate is suppressed in presence of $AlEt_3$ although

Table 1 Polymerization of IBVE by $POCl_3$–Et_3Al, $SOCl_2$–Et_3Al, V_2O_5–Et_3Al and t-BuCl–Et_3Al. Solvent, benzene

Experiment number	[IBVE] (mol/l)	[Et_3Al] (mol/l)	Initiator	[Et_3Al]/[Initiator]	Polymerization Temperature (°C)	Polymerization Time (min)	Conversion (%)	Index of stereo-specificity
1	1.25	0.001–0.2	none	–	0	180	No polymerization	
2	1.25	–	$POCl_3$/$SOCl_2$ (0.001–0.2 mol/l)	–	0 & 30	10	Charred mass	
3	1.25	0.05	$POCl_3$	0.5	30	20	22.4	5.0
4	0.625	0.125	$POCl_3$	2.5	30	1140	28.4	7.5
5	1.25	0.05	$SOCl_2$	0.5	30	30	55.5	2.4
6	1.25	0.05	$SOCl_2$	0.5	0	60	58.4	2.2
7	0.625	0.1	$SOCl_2$	1.0	30	60	39.5	4.0
8	0.625	0.125	$SOCl_2$	2.5	0	120	19.4	11.1
9	1.25	0.05	$SOCl_2$	0.5	30	180	85.1	0
10	0.83	0.066	$SOCl_2$	0.5	0	180	67.2	0
11	1.25	0.1	V_2O_5	0.5	30	1200	20.1	5.4
12	1.25	0.1	V_2O_5	2.0	30	1200	15.5	6.5
13	1.25	0.05	t-BuCl	0.5	30	120	44.3	0
14	0.625	0.1	t-BuCl	1.0	30	120	19.8	0
15	0.625	0.125	t-BuCl	2.5	30	120	10.8	0
16	1.43	0.028	t-BuCl	4.0	30	120	91.1	0

Aging was carried out with vigorous shaking for 5 min at 30°C. In experiments 3–8 and 11–15 IBVE and Et_3Al were aged first and then the initiator was injected. In experiments 9, 10 and 16 initiator and Et_3Al were aged followed by the addition of IBVE no stereoregularity has been observed in the product polymer.

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Correlation between fatigue fracture properties and viscoelastic damping response in engineering plastics

Early fatigue studies of engineering plastics identified a strong dependence of test frequency on fatigue life in unnotched test coupons[1–3]. Numerous investigators identified the onset of adiabatic heating in the gauge section as the primary cause for premature failure. In these cases, the elevated temperature associated with hysteretic heating increased the compliance of the test sample to the point where the cyclic loads could no longer be sustained, whereupon the sample literally melted. Analytical relationships were developed which revealed the temperature increase per loading cycle to be related to the loss compliance of the material, the stress level, test frequency and thermal properties of the polymer as described by equation (1)[4]:

$$\Delta\dot{T} = \frac{\pi f J''(f,T)\sigma^2}{\rho C_p} \qquad (1)$$

where $\Delta\dot{T}$ is the temperature change/unit time; f is the frequency (Hz); J'' is the loss compliance; σ is the peak stress; ρ is the density and C_p is the specific heat. It is pertinent to note that a relationship between fatigue response and viscoelastic properties (i.e. J'') was, therefore, identified for this type of failure.

When the fatigue crack propagation (*FCP*) rate of prenotched samples was examined, however, it was found that the test frequency had the opposite effect on cyclic response in poly (methyl methacrylate) (PMMA). Here, various investigators found that the crack growth rates under cyclic loading conditions decreased with increasing test frequency[5–8]. The implication associated with these earlier fatigue crack propagation studies was that the total crack growth rate was related in some way to a superposition of pure fatigue and pure creep components, respectively[9–12]. On the basis of these results certain crack propagation 'laws' were developed[11–13]. Since that time additional data have been reported which clearly demonstrate these laws to be premature in their formulation[9,14,15]. For example, PMMA, polystyrene and PVC experienced an attenuation in *FCP* rates with increasing test frequency while polycarbonate, nylon-6,6, and others showed no effect. It is worth noting that no material revealed higher crack growth rates with increasing frequency [recall equation (1)]. A number of hypotheses to account for this *FCP* frequency sensitivity have been examined and found wanting to various degrees[9]. One encouraging correlation, however, reported earlier by the authors, has been found between the relative *FCP* frequency sensitivity in several polymers and the frequency of movement of those molecular segments responsible for generating the beta transition peak at room temperature. It was found that the most frequency sensitive materials were those possessing a beta transition-related segmental jump frequency in apparent resonance with the applied machine test frequency. The authors suggested that this resonance condition contributed to a state of adiabatic heating local to the crack tip. This in turn was envisioned to soften the material, thereby blunting the crack tip radius. The more blunt crack tip, being less damaging to the material, would bring about a slowing down of the fatigue crack velocity under cyclic loading conditions.

This hypothesis could be critically examined in two ways. First, frequency insensitive engineering plastics could be made so by altering the machine test frequency range so as to bring the externally applied loading frequency in coincidence with the beta transition-related segmental jump frequency of the material. Since the beta-related jump frequency of materials such as polycarbonate, nylon-6,6 and poly(vinylidene fluoride) are of the order of 10^6 to 10^7, this approach is unreasonable owing to testing machine capability limitations. Alternately materials that were not *FCP* frequency sensitive at room temperature, might be made so at other temperatures if the altered segmental motion jump frequency of the material were now comparable to the mechanical test frequency. Indeed, this has been verified for polycarbonate and polysulphone under low temperature test conditions with maximum frequency sensitivity being found in polycarbonate and polysulphone at approximately 200K and 175K, respectively. Conversely, the very strong frequency sensitivity in PMMA found at 300K was eliminated when this material was tested at 150K. Preliminary results for polystyrene also confirm these trends.

It would appear then that the maximum frequency sensitivity to *FCP* in engineering plastics occurs at a particular temperature unique to that material. In each case that tem-