polymer communications

Bimolecular termination in living ring opening metathesis polymerization

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(*Received 12 August 1991*)

Previously observed high molecular weight impurities in the products of living ring opening metathesis polymerizations are identified as arising from a post-polymerization bimolecular dimerization initiated by dioxygen.

(**Keywords: ring opening metathesis polymerization; bimolecular termination**)

Introduction

Control of molecular weight distribution and the fine detail of molecular structure are important objectives in polymer synthesis. In chain growth polymerizations narrow molecular weight distributions may be obtained by the use of living processes, the key to success being the absence of any spontaneous chain termination reactions[1].

During the last few years several well defined transition metal complexes have been established as initiators for living ring opening metathesis polymerization (ROMP)[2–8]. These initiators contain either a metallacyclobutane or an alkylidene moiety and operate via the Chauvin mechanism[9]. All the indicators of well defined living polymerization processes have been demonstrated; thus, polymers with exceptionally narrow molecular weight distributions are usually obtained, there is direct proportionality between initiator to monomer ratio and molecular weight and block copolymers have been produced. Additionally, in favourable cases functionalized monomers can be polymerized and stereoregular polymers have been obtained.

Occasionally, we and other workers have observed small amounts of higher molecular weight material, usually constituting $<5\%$ of the sample, in the g.p.c. analyses of polymers made by living ROMP[10–14]. Grubbs and co-workers observed that this high molecular weight impurity usually occurred at twice the molecular weight of the major product, an observation which required that the process leading to it occurred either at the start or the end of the polymerization since a process occurring throughout the synthesis would lead to a broadening of the molecular weight polydispersity rather than the bimodal distribution observed[13,14]. Here we provide an explanation for the formation of this by-product in terms of a bimolecular termination reaction with trace amounts of dioxygen present in the monomer feed.

Results and discussion

This general phenomenon is exemplified in the outcome of the polymerization of an endo/exo mixture of 5-trifluoromethylbicyclo[2.2.1]heptene initiated by Mo(NAr)(CH-t-Bu)(O-t-t-Bu)$_2$, where Ar = 2,6-diisopropylphenyl, and terminated by addition of benzaldehyde. The g.p.c. trace for the resultant polymer is shown in *Figure 1*; it is clearly bimodal and within the limits of the accuracy of the analysis the minor peak occurs at a retention volume corresponding to material with twice the molecular weight of the major peak. Significantly, we can see that the minor peak is observed only in the trace using refractometer detection, indicating that the u.v. active phenyl group arising from the capping reaction is not present in the high molecular weight component, and that both peaks have similar narrow molecular weight distributions. Taken together these observations are consistent with the hypothesis that the high molecular weight component was formed after the polymerization was complete by a dimerization of living chains.

In a programme of work designed to test the stability of metal alkylidenes towards dioxygen[15] the complex of interest in this work, Mo(NAr)(CH-t-Bu)(O-t-Bu)$_2$, was treated with O_2 (1 atm) in a sealed tube. The reaction was monitored by n.m.r. spectroscopy and proceeded quite slowly (several hours) to give Mo(O)(NAr)(O-t-Bu)$_2$ and pivaldehyde (equation (1)) which was

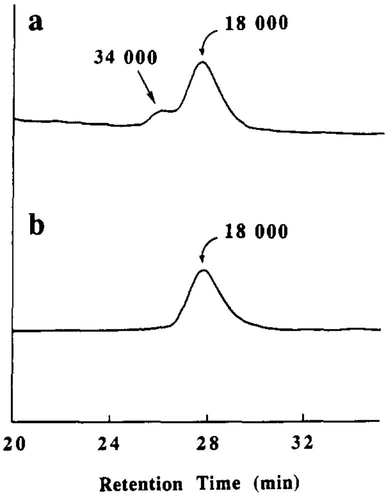

Figure 1 Gel permeation chromatograph of poly(5-trifluoromethylnorbornene) recorded for a 0.3% solution in CH_2Cl_2 using a P$_{gel}$ three-column set covering the 10^3–10^6 amu range (Polymer Laboratories) and a refractometer (a) and a u.v. detector (b) in series. Molecular weights are polystyrene equivalent number average values

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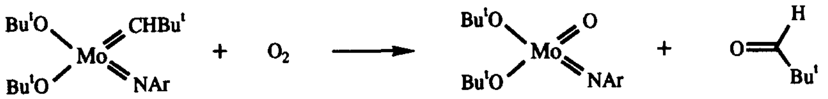
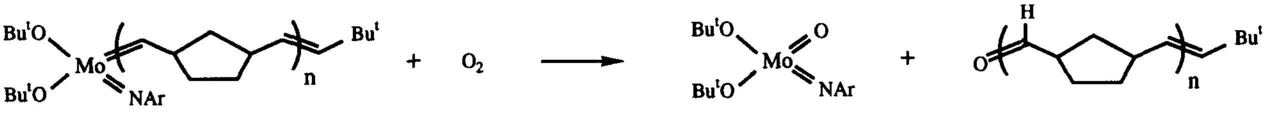

(1)


(2)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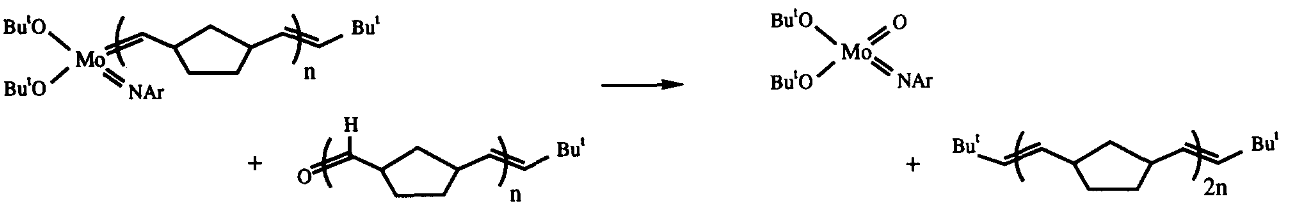
(4)

subsequently observed to react with the starting alkylidene complex to generate *trans*-2,2,5,5-tetramethylhex-3-ene (equation (2)).

In a related experiment we have reacted norbornene (10 equivalents) with Mo(NAr)(CH-t-Bu)(O-t-Bu$)_2$ to generate living polynorbornene oligomers which were then exposed to O_2 as described above; a reaction occurred over a period of minutes giving the oxo-imido species, an observation which can be rationalized according to equations (3) and (4). The reaction between O_2 and the alkylidenes of the living oligomers is slower than the rate of propagation although it is much faster than the rate of reaction with the initiator. A possible alternative rationalization, based on the fact that transition metal oxo species can react with alkylidenes to give products arising from coupling of the alkylidene ligands[15], can be ruled out as an explanation of the origin of the molecular weight doubling side reaction under discussion here because it has been found that the amount of high molecular weight product formed can be reduced or entirely eliminated by redistillation of monomers under an atmosphere of N_2 immediately prior to polymerization and rigorous exclusion of dioxygen.

We have observed that this molecular weight doubling phenomenon is particularly prevalent in our work on fluorinated monomers; an observation consistent with the greater solubility of dioxygen in such media. However, the phenomenon is by no means universal and, for example, where the γ-carbon in the living alkylidene oligomers carries a trifluoromethyl substituent, as in the living polymer from 2,3-bis(trifluoromethyl) norbornadiene, high molecular weight contaminants are not observed, a fact consistent with steric inhibition of the dimerization at the metal centre in the process shown in equation (4).

Acknowledgements

We thank the SERC for a grant and studentships (JPM and ELM), the SCI for a Messel Scholarship (JPM) and Professor R. R. Schrock for stimulating discussions.

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