STEREOREGULATION DURING THE OLIGOMERIZATION OF

TRITYL METHACRYLATE[1]

G. Wulff[*], R. Sczepan, and A. Steigel

Institute for Organic Chemistry II, University of
Düsseldorf, Universitätsstr. 1, D-4000 Düsseldorf, F. R. G.

*For the first time, uniform optically active oligomers of methyl methacrylate with degrees
of polymerization (DP) = 1, 2, 3, and 4 were obtained by the anionic polymerization of trityl
methacrylate using 1,1-diphenylhexyl lithium/(-)sparteine, followed by the substitution of
trityl for methyl, and subsequent g.p.c. separation. The mechanism for the formation of
optically active poly(trityl methacrylate) is discussed in this paper.*

Okamoto and coworkers[3,4] have reported the synthesis of optically active poly(trityl meth-
acrylates) by anionic polymerization of trityl methacrylate in toluene at -80°C using butyl
lithium/(-)sparteine as the optically active initiator system. The origin of the optical
activity of this polymer has been attributed to the formation of a rigid single sense helix
conformation stabilized by bulky trityl groups. Optical activity $[\alpha]_D^{20}$ to the extent of +300°
was realized with these polymers.

The poly(trityl methacrylate) thus obtained was transformed to poly(methyl methacrylate)
by hydrolytic cleavage of the trityl groups and subsequent methylation with diazomethane.
This polymer did not exhibit any optical activity. It was highly isotactic and possessed a
random coil conformation in solution. So it appears,optical activity in poly(trityl meth-
acrylate) was brought about by a type of atropisomerism[3,4].

It remains unclear whether during the formation of optically active poly(trityl meth-
acrylate) all the chiral centers generated along the polymer chain possess the same absolute
configuration. This question cannot be answered by investigating the isotactic polymers
since quasi-meso compounds exist[5]. In contrast, oligomers do not form quasi-meso structures;
hence examination of the oligomers formed during the early steps of polymerization ought to
be able to unravel this mystery. Furthermore, it was anticipated that characterization of the
oligomeric species would provide deeper insight into the stereoregulation process as well as
suggest a plausible mechanism for the formation of the helix.

It has already been observed by Okamoto et al.[6] that during the formation of optically
active poly(trityl methacrylates) a substantial amount of oligomers were invariably formed.
Since under the reported reaction conditions[3,4] some by-products were formed by the attack
of the initiator on the carbonyl group, we have employed a more selective initiator system

consisting of 1,1-diphenylhexyl lithium/(−)sparteine to inhibit the formation of by-products. Nevertheless a substantial amount of the active centers remained in the oligomeric state. These oligomers were present in the form of living anions in the reaction medium as evident from our termination experiments using tritium acetate. Nearly 40% of the active species were unable to grow further and remained in oligomeric form till the end of the polymerization. The oligomers thus obtained were characterized and compared with those obtained by polymerization using smaller monomer/initiator ratios where a predominant formation of oligomers takes place.
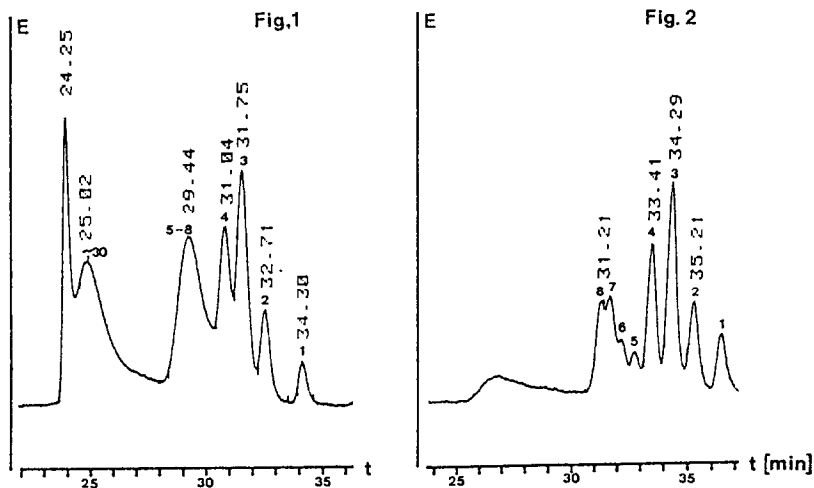
Legend: G.p.c. separation of oligomers obtained with a monomer/initiator ratio of 5:1. Fig. 1 trityl, Fig. 2 methyl esters. Column: Two columns 600 mm lenght, 7 mm i.d. with P.L.-gel (50 Å), and P.L.-gel (100 Å), resp. Solvent: THF, Detector: UV (251 nm). Flow: 0.8 ml/min.

A g.p.c. separation curve of the oligomers of trityl methacrylate obtained with 5:1 monomer/initiator ratio and terminated with methanol is shown in Fig. 1. The chromatogram of the methyl methacrylate oligomers obtained from the trityl derivatives (Fig. 1) by hydrolysis and reesterification is depicted in Fig. 2. A similar distribution pattern was also observed for the oligomers obtained with higher monomer/initiator ratios. The only difference in the latter case being the formation of a large amount of high molecular weight species, in addition to the oligomers.

The oligomers obtained with different monomer/initiator ratio (from 1:1 to 10:1) were fractionated by means of preparative g.p.c. (10 μm particles of a styrene-divinylbenzene resin obtained from Dr. M. Minárik, Prague, solvent: tetrahydrofuran). Trityl methacrylates (DP=1 and 2) and the corresponding methyl methacrylates obtained from trityl derivatives with DP = 1, 2, 3 and 4 were all obtained in a uniform state, whereas oligomers having DP = 5-8 were obtained as a mixture.

With the aid of high resolution ^{1}H and ^{13}C-n.m.r. spectroscopy[7], it was possible to elucidate in detail the configuration of these oligomers. The composition of the mixture of the diastereoisomers of these oligomers was determined and is presented in Scheme 1. It is interesting to note that excepting the last asymmetric center of the chain, the oligomers show isotactic chain structures. The last asymmetric center of the oligomers is generated as a result of termination with a proton. This process being non-stereoselective, the

configuration of the end asymmetric carbon atom is independent of the stereochemistry of the chain propagation.

The results of the optical activities of the oligomers of trityl and methyl methacrylate are summarized in Table 1. In contrast to the strong positive optical rotation of poly (trityl methacrylate), the oligomers showed predominantly negative rotation. This is the first report on the study of methacrylate-based optically active oligomers. The optical activity of the oligomers was found to be dependent on the feed monomer/initiator ratio. At a lower ratio, the optical rotation was found to be more positive in all cases. This suggests that at higher monomer/initiator ratios (with higher conversion to high molecular weight
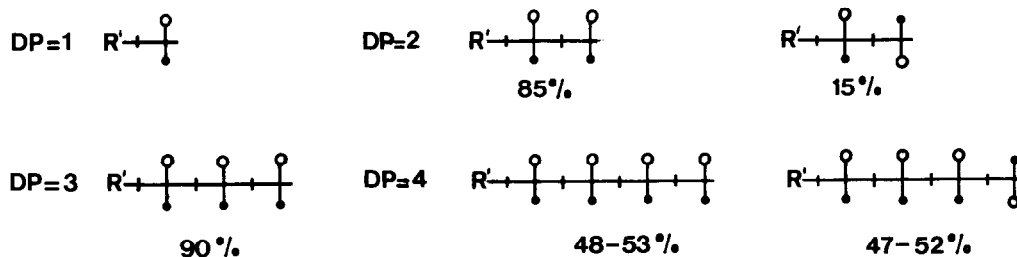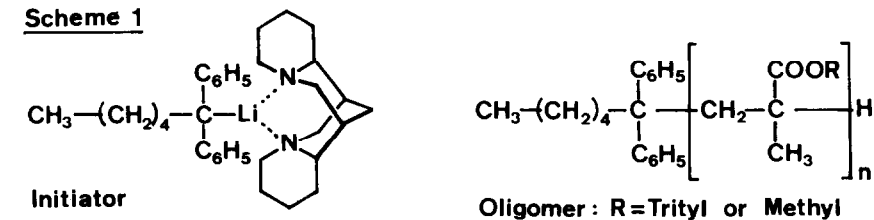
Scheme 1

Initiator

Oligomer : R = Trityl or Methyl

DP=1   DP=2   85%   15%

DP=3   90%   DP≧4   48–53%   47–52%

Table 1.   Optical Activity of Oligomers

DP	$[\alpha]_D^{20}$ of oligomers of			
	trityl methacrylate		methyl methacrylate	
1	$+10°$[a]		$+8°$	
2	-11	$- \ -14°$	-10	$- \ -18°$
3	$- 7$	$- \ - 9°$[b]	-11	$- \ -28°$
4	$- 8$	$- \ -10°$[b]	$+ 4$	$- \ -10°$
5–8	-23	$- \ -31°$[b]	$+ 7$	$- \ + 9°$
30	$+303°$		$0°$	

Range of optical activity of oligomers prepared with different monomer/initiator ratio. a) DP = 1 was only isolated from reaction mixtures with monomer/initiator ratio of 1:1. b) Optical activity determined after g.p.c separation by simultaneous detection with an u.v.-de-tector and a polarimeter detector.

substances), the more positively rotating isomers react relatively faster with the monomers. As a consequence, the reaction mixture becomes enriched with the more negatively rotating oligomeric species.

With regard to the mechanism of the formation of helical poly(trityl methacrylate) in the presence of optically active initiator systems the following conclusions may be drawn:

a) The addition of the first monomeric unit of trityl methacrylate to the initiator system is brought about with certain amount of asymmetric induction.

b) Even during the oligomerization process, chain growth takes place predominantly in isotactic fashion. From this the formation of two enantiomeric isotactic chains, each possessing a different propagation rate is evident.

c) Growth of the helix is likely to proceed only with identical chain configuration in a manner similar to the helix control-mechanism, proposed by Doty and Lundberg[8].

d) The oligomer distribution curves (Fig. 1 and 2) show a trimodal distribution pattern, wherein the presence of three groups of species can be readily recognized. While the first group consists of 4 species (DP = 1-4), the second group comprises of oligomers having DP = 5-8. The third group of oligomers is found only in the range of DP = 20-40 and surprisingly, substantial amounts of oligomers are not found in the range between the DP = 5-8 to DP = 20-40. This study merits further investigation to confirm our present understanding of the influence of the possible conformation of the oligomers (one turn of a helix at DP = 4 and two turns at DP = 8) on the propagation rate.

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