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Thermal Stability

Thermal Stability of Poly(Methyl Methacrylate)

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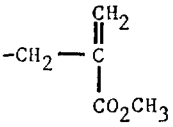
SUMMARY

The average solid-state molecular structures of end-groups generated through chain termination reactions in the polymerization of methyl methacrylate have been derived from published crystallographic data. Evidence is provided for the reduced stability of the head-head chain-termination configuration and in support of the postulate that it is a preferred site of chain scission. Comparable evidence for the unsaturated end group has not been found.

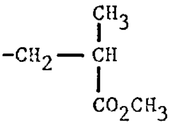
INTRODUCTION

Thermal stability studies have been carried out recently [1] on model compounds which possess molecular configurations equivalent to those formed through the chain termination reactions in the free radical polymerization of methyl methacrylate. The observations provide some evidence that the well-established two-stage thermal degradation of poly(methyl methacrylate) [2] is a consequence of the lower stability, compared to the polymer itself, of the anomalous fragments introduced into the polymer by disproportionation and head-head termination of the radical chains (I-III).



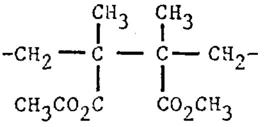
$-CH_2-C(=CH_2)-CO_2CH_3$

I



$-CH_2-CH(CH_3)-CO_2CH_3$

II



$-CH_2-C(CH_3)(CO_2CH_3)-C(CH_3)(CO_2CH_3)-CH_2-$

III

This communication reports the results of a search and an analysis of the solid-state structural data reported in the crystallographic literature which is pertinent to the problem. The study was undertaken firstly to determine the average structure and conformation of the various molecular fragments (I-III); and secondly to seek evidence of bond strain as manifest in structural perturbations and to correlate it with the observed behaviour of the polymer.

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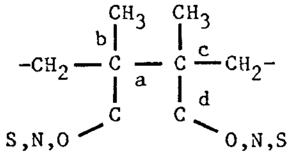
RESULTS AND DISCUSSION

The numerical data base (CSD) was that assembled by the Cambridge Crystallographic Data Centre [3]. The version used was dated February 1984 and contained single-crystal structural data on 36,418 organic compounds. It is on file through the Australian Affiliated Centre at the Central Information Service, CSIRO.

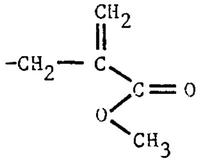
Head-head Link

The central question we attempted to resolve was that of strain at the head-head link (III). Cacioli et al propose that this configuration constitutes the least stable group arising from the polymerization termination reactions. As such it implies that a head-head link within the poly(methyl methacrylate) molecule is a favoured nucleating site for chain degradation.

A search for the specific fragment (III) was unrewarding. The conditions were relaxed to the fragment (IV) and allowance made for its inclusion as part of a ring system.



IV



V

This survey yielded 12 compounds. Several structures were eliminated on the basis of accuracy (R>0.09), and the presence of disorder [4]. Two additional structures were excluded for reasons given below to leave six structures with CC bond lengths for which $\sigma_{cc}<0.014$ Å. The bond lengths observed are summarized in Table 1.

Table 1

Compd.	Midbond	Methyl Group		Methylene Group		C-C(O,N,S)		Ref
	"a"	"b"		"c"		"d"		
HMCDCO	1.547 Å	1.541 Å	1.527 Å	1.547 Å	1.533 Å	1.537 Å	1.517 Å	[5]
HNPHLN	1.551	1.536	1.554	1.533	1.542	1.529	1.536	[6]
HTMXTB	1.549	1.536	1.538	1.533	1.545	1.527	1.535	[7]
HTMXTC	1.547	1.541	1.537	1.536	1.531	1.522	1.532	[7]
HTMXTD	1.563	1.549	1.543	1.536	1.521	1.504	1.509	[8]
MEXMBN	1.553	1.521	1.527	1.547	1.545	1.524	1.531	[9]
OHMEDC	1.556	1.533	1.541	1.545	1.541	1.520	1.560	[10]
Mean	1.552(5)	1.538(8)	1.538(9)	1.540(6)	1.537(8)	1.523(9)	1.531(15)	
		Mean	1.538(8)			1.527(12)		

The CC bond with the hetero-atom substituent (IV,d) shows the expected bond shortening from the paraffinic value of 1.541 Å. No significant difference is shown between the methyl (IV,b) and methylene (IV,c) bonds attached to the central carbon atoms. They may be combined to give the average figure of 1.538(8) Å.

The midbond (IV,a) thus exhibits an extension of 0.014Å and in consequence provides supporting evidence for strain at that location.

In the examples selected the methyl groups are all in a minimum energy conformation with the torsion angle between methyl groups of ±60° or 180°. One of the additional structures (PMXCDO [11]) excluded from the averages has strain introduced by virtue of a rigid molecular framework. In that case the torsion angle is reduced to 33.7° and the bond lengthened to 1.585Å. The second of these structures (BUFNUL [12]) has a straight chain configuration with the central bond across a centre of symmetry. This may result in the introduction of additional systematic errors and the structure was excluded on this basis. The bond length quoted was 1.618Å.

Both the latter structures emphasize the bond extension but even without their inclusion the evidence points clearly to the strained nature of the bond introduced into the poly(methyl methacrylate) molecule through the head-head chain termination reaction with concomitant susceptibility to fission at that point.

End Groups

Schweizer and Dunitz [13] have studied in considerable detail the structural variations to be found in the carboxylic ester group which forms a sub group of our search fragment. Our results affirm that the methyl group is found exclusively in the Z conformation in which the O-methyl bond is cis (within ±10°) to the carbonyl C=O bond (Table 2).

A search was made additionally for the fragment V which combines both the ethenyl and the carboxylic ester group. All bonds were restricted to being acyclic to ensure reasonable compatability with a polymer end group. This search yielded six structures with acceptable accuracy. Table 2 itemizes the structural features of interest. They are the torsion angle of the ester group, the torsion angle between the C=O and C=C bonds and the length of the linking bond between those functional groups.

Table 2

Compd.	Ester Group Torsion angle O=C-O-C	Unsaturated Group Torsion angle C=C-C=O	Bond Length (C=C)-(C=O)	Ref
ACROLD	2.2°	-178.3°	1.472Å	[14]
BEFHEZ	3.3	-173.1	1.479	[15]
BIPRUN	-11.8	-15.2	1.491	[16]
BOWTAI	-6.5	172.2	1.492	[17]
GLAUCA	5.0	166.5	1.486	[18]
RADIAT	-10.5	-30.3	1.470	[19]
		Mean	1.482(9)	

The linking bond is significantly shorter than the corresponding bond in fragment III ("d" of Table 1). The magnitude of the change is comparable to that found with aromatic substituents (1.484(12)Å)[13].

The unsaturated end group shows no preference for any particular conformation. In so far as it may be equated to part of an aromatic ring the ethenyl group when in conjunction with the carboxylate group adopts the anticipated conformation [13]. At the same time, there is no tendency for the C=C bond to align preferentially, either cis or trans, with the carbonyl.

CONCLUSION

To the extent it is possible to establish essentially dynamic properties from static structures we have shown that there is structural evidence in support of the ideas that polymer chain degradation is initiated at head-head junctions in preference to the normal polymer link. No information has been found as to the relative stability of this arrangement and the saturated and unsaturated end groups.

As to whether the structural features are the initiating sites by virtue of their intrinsic characteristics or merely represent molecular features which allow concentration of thermal energy at specific sites would require detailed study using more appropriate techniques [20].

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