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# SOME ASPECTS OF THE CHEMISTRY AND PHYSICS OF DENTAL RESINS

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## ABSTRACT

The status of denture-base poly(methylmethacrylate) (PMMA) has been reviewed, and in spite of the availability of mechanically superior injection-molded resins, it remains the material of choice. PMMA can be reinforced with fibers, the most recent being ultra-high-modulus polyethylene fibers. Various elastomer reinforced materials are also available. Alternatives to room-temperature polymerizing PMMA resins include higher methacrylates and epimine resins. High-modulus resins have been produced with Bisphenol A-glycidyl methacrylate (BisGMA) and tetrahydrofurfuryl methacrylate, involving an anti-plasticizer function. Also reviewed are room-temperature polymerizing initiators, radio-opaque resins, and studies on polymerization shrinkage.

## INTRODUCTION

This paper reviews the main uses of resins in dentistry *excluding* their use in composite materials. The first six sections deal with resins *per se*, the next with initiators, and the last section with the general subject of polymerization shrinkage.

## DENTURE-BASE RESINS

### *Poly(methyl methacrylate) – PMMA*

PMMA has been the principal denture-base resin now for some 45 years, mainly fabricated as a dough following the original patent of the Kulzer Company (1938). Its ease of fabrication with very simple equipment has ensured its survival in spite of well-documented defects with respect to strength, both impact and fatigue. (In the United Kingdom, for example, it is estimated that about 800,000 denture repairs are undertaken by the Department of Health and Social Security *per annum* [Stafford *et al.*, 1980], and this of course does not include repairs undertaken privately.) With respect to fatigue, it is interesting to note that a fundamental study of the fatigue of PMMA showed that its fatigue life dry was some five times greater than when it contained 1% water!

Possibly more serious than the defects of PMMA

*per se*, are the problems that arise when it is improperly processed. Studies of PMMA dentures in service, particularly those from patients presenting symptoms, revealed that some contained residual monomer levels up to 12%, instead of a value of 0.5% (Austin and Basker, 1980). Dentures with high residual monomer can, of course, have adverse effects on the oral mucosa, apart from the effects of a highly depressed glass transition temperature. Adverse reaction to PMMA-based dental materials have also been cited by Ruyter (1979), Weaver and Goebel (1980), Fernström and Øquist (1980), and Hensten-Pettersen and Victorin (1981).

Various methods have been used to improve the strength of PMMA, and there are a number of high-impact-strength acrylics available that utilize reinforcement by the incorporation of an elastomer into the polymer powder (Dentsply, 1969). Stafford *et al.* (1980) have reviewed the properties of such materials, and Rodford (1986) has described a new elastomeric system. An alternative method is to use reinforcing fibers. Early papers describe the use of carbon (Schreiber, 1971; Manley *et al.*, 1979). More recently ultra-high-modulus polythene (UHMPE) fibers have been used successfully to reinforce denture-base resins (Braden *et al.*, 1988). Table 1 lists some typical properties. The UHMPE fibers are completely unobtrusive in the resin, and thus are completely esthetic.

### *Alternatives to PMMA*

In an attempt to overcome the mechanical and possible allergic defects of PMMA, investigators have used

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success among dentists in Europe over the last decade or so. However, the chief reason for its inclusion here is to draw attention to the possibilities of non-free-radical polymerizing initiator systems.

### HEAT-CURED BIS GMA SYSTEM

Bis phenol A-glycidyl methacrylate (BisGMA) and related dimethacrylates are inevitably associated with composite filling materials and fissure sealants, and hence with room-temperature polymerization. However, studies have been made of heat-polymerized Bis GMA, and the effects of various diluent monomers. Rather surprisingly, one monomer (tetrahydrofurfuryl methacrylate) had an enhancing effect on modulus (Fig. 2); at 5% THFM v/v, a modulus of about 5 GPa is achieved. Poly(THFM) itself has a modulus of 2 GPa, and so THFM with Bis GMA is acting as an anti-plasticizer. With other diluents (as yet undisclosed because of the patent situation), moduli approaching 6 GPa have been achieved.

The modulus of most glassy linear polymers is about 3 GPa, although values of 6 GPa can be obtained on such polymers with high-frequency visco-elastic measurements, when the rate of deformation is high enough to suppress secondary relaxation processes.

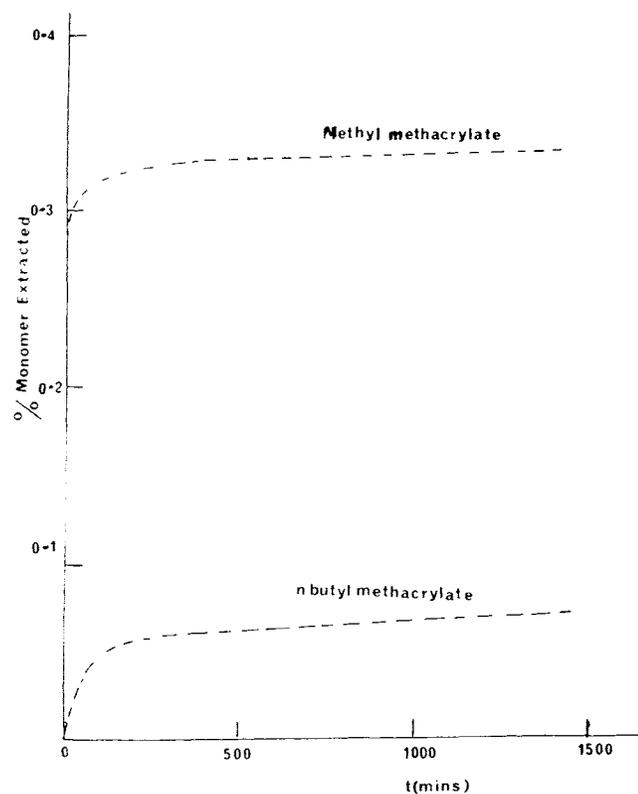


Fig. 1—Comparison of extraction of n-butyl methacrylate and methyl methacrylate monomers from room-temperature polymerizing systems.

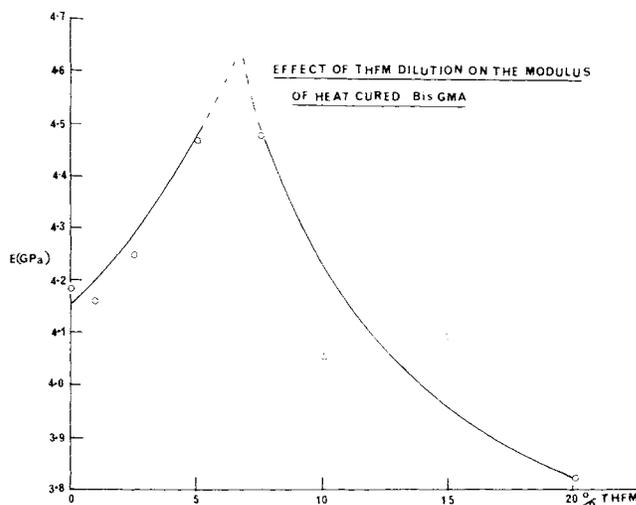


Fig. 2—Modulus of elasticity of heat-polymerized Bis GMA as a function of concentration of tetrahydrofurfuryl methacrylate.

Hence, it is inferred that the high modulus obtained in the above systems at low rates of deformation is due to very efficient coefficient cross-linking, inhibiting secondary relaxation processes.

Analogous experiments have been carried out on related Bis GMA materials, but without hydroxyl groups, and none has given the high moduli obtained with Bis GMA.

Uni-axial reinforcement by bundles of fibers of the anti-plasticized resins described above has achieved moduli of  $\approx 30$  GPa and very high flexural strengths.

Current work is examining reinforcement by short staple fibers.

### ROOM-TEMPERATURE POLYMERIZATION INITIATING SYSTEMS

The most common system is still the peroxide-amine system, *e.g.*, benzoyl peroxide-*NN* dimethyl *p* toluidene; the rather complex chemical mechanism has been described by O'Driscoll and Ghosh (1969). It has the well-known disadvantages of discoloration, oxygen inhibition, and relatively poor conversion. Alternative systems utilize:

- (i) *p* toluene sulfinic acid (Brauer and Burns, 1956), usually present as a salt in the polymer powder, and released by methacrylic acid in the monomer component;
- (ii) trialkyl borane systems (Ida *et al.*, 1975); and
- (iii) benzoyl peroxide-ascorbic acid (Antonucci *et al.*, 1979).

These are, of course, all free-radical systems; the epimine system described previously is cationic and would seem to merit further study.

TABLE 2  
DENSITY AND SHRINKAGE DATA FOR Bis GMA-BASED DIMETHACRYLATES

Monomer	Density (g/cc)		Molar Volume ( $V_m$ cc/mol)		Shrinkage ( $\Delta v/v\%$ )	$\Delta V_m^*$	% Conversion
	Monomer	Polymer	Monomer	Polymer			
A	1.175	1.237	413.62	312.89	5.3	20.73	47%
B	1.121	1.200	397.86	371.67	7.04	26.19	59%

A - 2,2 bis 4(2 hydroxy-3-methacryloyloxy propoxy)phenyl propane.

B - 2,2 bis 4(2 methacryloyloxy ethoxy) phenyl propane.

\*Since these are difunctional monomers, this value should be twice the  $\Delta V_m$  of monofunctional monomers, i.e., 44.

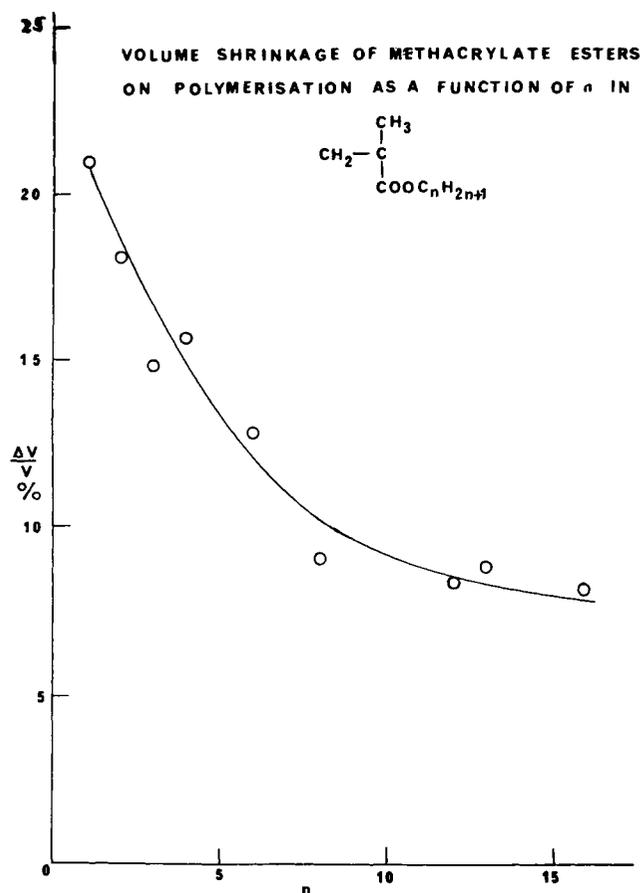


Fig. 3—Polymerization shrinkage as a function of the number of carbon atoms ( $n$ ) in the ester side-chain of  $n$ -alkyl methacrylates.

## RADIO-OPAQUE ACRYLICS

Since the inception of PMMA dentures, difficulties in the location and removal of aspirated fragments have been reported (Drinnan, 1967). Hence, there have been a host of reagents used to confer radio-opacity. Two more recent and novel approaches are those of Davy and Causton (1982) and Ahir and Foster (1972). The former uses brominated methacrylate polymers and the latter alkyl tin methacrylates.

MOLAR VOLUME OF MONOMER UNIT  
AS A FUNCTION OF  $n$  IN

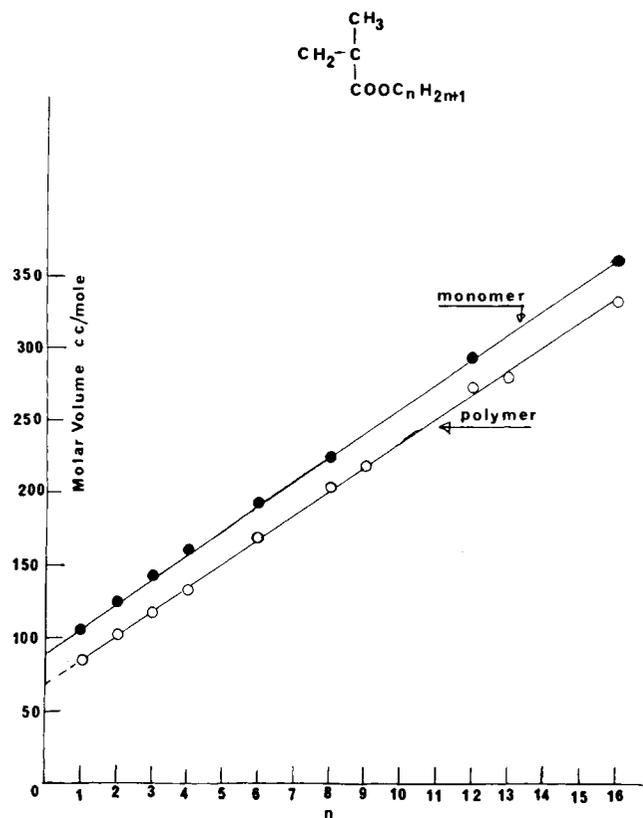


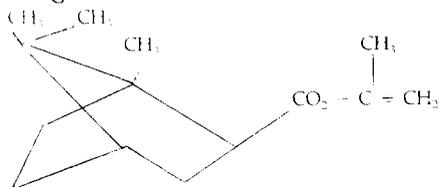
Fig. 4—Plot of molar volumes of  $n$ -alkyl methacrylate monomers and polymers as a function of the number of atoms ( $n$ ) in the ester side-chain.

## POLYMERIZATION SHRINKAGE

Shrinkage is a major problem with polymerizable systems, and indeed a major *raison d'être* for the development of composites was to reduce polymerization shrinkage. Detailed consideration has been given in the literature to ring-opening polymers (Thompson *et al.*, 1979) to give zero shrinkage or even expansion.

A detailed study here of a wide range of monofunctional methacrylates has shown that, first with  $n$

alkyl methacrylates, volume shrinkage decreases with the size of the substituent alkyl group (Fig. 3). However, if molar volumes of monomers and polymers are compared (Fig. 4), it is clear that the change in molar volume is constant at about 22 cc/mol; indeed this value of molar volume change was found to apply to a very wide range of mono-functional methacrylates, including cyclic and heterocyclic methacrylates. Hence, the lower shrinkage of, say, isobornyl methacrylate ( $\approx 10\%$  by volume) is merely due to the fact that there are fewer molecules *per* unit volume. Of course, as one ascends the *n* alkyl series, the  $T_G$  descends rapidly and the  $C_6$  polymer is a rubber. However, heterocyclic and cyclic methacrylates of molar volume comparable with that of elastomeric alkyl methacrylates are in fact glassy polymers, albeit of  $T_G \approx 40 - 60^\circ\text{C}$ . Hence, while the volume of the ester group governs shrinkage, its shape is very important as far as  $T_G$  is concerned. The most striking example of this is isobornyl methacrylate, with a molar volume similar to that of a  $C_{12}$  alkyl ( $T_G \approx 60^\circ\text{C}$ ) yet with a  $T_G$  of  $\approx 100^\circ\text{C}$ .



The comparison of experimental changes in molar volume with the value 22 cc/mol can be used to determine the degree of polymerization (Patel *et al.*, 1987). Bis GMA, for example, even heat-cured, has a conversion of only 47% (Table 2).

## THE FUTURE

It appears that there is still much scope for systematic investigations into the relationship between molecular structure and properties of clinical importance such as shrinkage, strength, and water absorption.

There still appears to be a need for a satisfactory soft lining material, and for radio-opaque polymers.

There is considerable scope for more efficient room-temperature polymerizing systems for all types of resins.

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