

Industrial Polymers Handbook

Products, Processes, Applications

Edward S. Wilks (Editor)

Volume 2

Synthetic Polymers (Continued)

 **WILEY-VCH**

Weinheim · New York · Chichester · Brisbane · Singapore · Toronto

Dr. Edward S. Wilks (Editor)
E. I. du Pont de Nemours & Co. Inc.
CR&DD-BMP-14-1288
P. O. Box 80014
Wilmington, DE 19880-0014
USA

This book was carefully produced. Nevertheless, editor, authors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Cover Illustration: Poly[5-[phenoxytris(ethoxy)carbonyl]bicyclo[2.2.1]hept-2-ene] was prepared via ring-opening metathesis polymerization of the corresponding monomer in the presence of bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride. This thermally stable functionalized polynorbornene has a thermogravimetric decomposition temperature of 431°C. Reproduced by courtesy of Professor Alaa S. Abd-El-Aziz, University of Winnipeg, Canada.

Library of Congress Card No. Applied for.

British Library Cataloguing-in-Publication Data: A catalogue record for this book is available from the British Library.

Deutsche Bibliothek – CIP Cataloguing-in-Publication-Data:

A catalogue record for this publication is available from Die Deutsche Bibliothek.

ISBN 3-527-30260-3

© WILEY-VCH Verlag GmbH, D-69469 Weinheim (Federal Republic of Germany), 2001

Printed on acid-free paper.

All rights reserved (including those of translation in other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition: Rombach GmbH, D-79115 Freiburg
Printing: Strauss Offsetdruck GmbH, D-69509 Mörlenbach
Bookbinding: Wilhelm Osswald & Co., D-67433 Neustadt (Weinstraße)
Cover Design: Gunther Schulz, D-67136 Fussgönheim
Printed in the Federal Republic of Germany.

Industrial Polymers Handbook

Edward S. Wilks (Editor)

Volume 2

 **WILEY-VCH**

Industrial Polymers Handbook

Edward S. Wilks (Editor)

- Volume 1 Polymerization Processes
 Synthetic Polymers
- Volume 2 Synthetic Polymers (Continued)
- Volume 3 Synthetic Polymers (Continued)
 Biopolymers and their Derivatives
- Volume 4 Biopolymers and their Derivatives (Continued)
 Indexes

Contents

4	Polymethacrylates	619
4.1.	Introduction	619
4.2.	Properties	620
4.3.	Raw Materials	623
4.4.	Production Processes	624
4.5.	Uses	630
4.6.	Toxicology	636
4.7.	Environmental Aspects	637
4.8.	References	637
5	Polyolefins	641
5.1.	Polyethylene	643
5.2.	Polypropylene	692
5.3.	Poly(1-Butene)	739
5.4.	Polyisobutylene	750
5.5.	Poly(4-Methyl-1-Pentene)	760
5.6.	References	777
6	Polystyrene and Styrene Copolymers	789
6.1.	Polystyrene	790
6.2.	Styrene – Acrylonitrile (SAN) Copolymers	804
6.3.	Barrier Resins	812
6.4.	Other Copolymers	814
6.5.	Acrylonitrile – Butadiene – Styrene (ABS) Polymers	816
6.6.	References	857
7	Poly(Vinyl Chloride)	865
7.1.	Introduction	865
7.2.	Physical and Chemical Properties	867
7.3.	Resources and Raw Materials	868
7.4.	Production	869
7.5.	Environmental Protection	896
7.6.	Quality Specifications and Analysis	897
7.7.	Storage and Transportation	897
7.8.	Processing and End Uses	898
7.9.	Economic Aspects	900
7.10.	Toxicology and Occupational Health	902
7.11.	References	903
8	Poly(Vinyl Esters)	907
8.1.	Introduction	907
8.2.	Raw Materials	908
8.3.	Polymer Structure	910
8.4.	Production	911
8.5.	Industrially Important Poly(Vinyl Esters)	915
8.6.	Properties	916
8.7.	Quality Specifications, Trade Names, Storage and Transport, Wastewater	918
8.8.	Uses, Toxicology, and Economic Aspects	919
8.9.	References	921

9	Poly(Vinyl Ethers)	923
9.1.	Introduction	923
9.2.	Production	924
9.3.	Industrial Processes	925
9.4.	Properties and Uses	926
9.5.	Copolymers	928
9.6.	Toxicology	928
9.7.	References	929
10	Poly(Vinylidene Chloride)	931
10.1.	Introduction	931
10.2.	Production	932
10.3.	Structure and Properties	937
10.4.	Processing and Uses	941
10.5.	Economic Aspects	948
10.6.	Toxicology and Occupational Health	949
10.7.	References	949
11	Other Polyvinyl Compounds	953
11.1.	Poly(Vinyl Alcohol)	953
11.2.	Poly(Vinyl Acetals)	960
11.3.	Poly(N-Vinyl lactams) and Poly(N-Vinyl amines)	968
11.4.	References	973
4	Polymers Formed by the Opening of a Multiple Bond Other Than a Carbon-Carbon Bond	979
I	Polyoxymethylenes	981
1.1.	Introduction	981
1.2.	Physical and Chemical Properties	983
1.3.	Production	988
1.4.	Economic Aspects	993
1.5.	Quality Specifications and Analysis	994
1.6.	Product Range and Processing	994
1.7.	Uses	995
1.8.	Recycling	996
1.9.	Toxicology and Occupational Health	996
1.10.	References	996
5	Polymers Formed by Ring-Opening Reactions	1001
I	Polyaziridines	1003
1.1.	Monomers	1003
1.2.	Homopolymers	1003
1.3.	Polymers Modified by Aziridine Grafting	1004
1.4.	References	1004

2	Polyoxyalkylenes	1005
2.1.	Introduction	1005
2.2.	Properties	1006
2.3.	Production	1011
2.4.	Toxicity	1014
2.5.	Handling	1015
2.6.	Uses	1016
2.7.	Economic Aspects	1017
2.8.	References	1018
3	Metathesis Polymers	1023
3.	Metathesis Polymers	1023
3.1.	References	1025
6	Synthetic Resins	1001
I	Alkyd Resins	1029
1.1.	Introduction	1029
1.2.	Production	1032
1.3.	Chemistry of Film Formation	1041
1.4.	Modified Alkyds	1043
1.5.	Low-Solvent Coatings	1045
1.6.	Markets and End Uses	1047
1.7.	References	1049
2	Amino Resins	1053
2.1.	Introduction	1053
2.2.	Physical Properties	1054
2.3.	Chemical Properties	1055
2.4.	Raw Materials	1056
2.5.	Production	1059
2.6.	Environmental Protection	1070
2.7.	Types of Resins and Their Properties	1071
2.8.	Analysis	1081
2.9.	Storage and Shipment	1082
2.10.	Uses	1083
2.11.	Economic Aspects	1093
2.12.	References	1094
3	Epoxy Resins	1099
3.1.	Introduction	1100
3.2.	Types of Epoxy Resins	1101
3.3.	Curing and Processing Technology	1111
3.4.	Uses	1117
3.5.	Economic Aspects	1121
3.6.	Toxicology and Occupational Health	1122
3.7.	References	1124
4	Phenolic Resins	1129
4.1.	Introduction	1129
4.2.	Physical Properties	1133
4.3.	Raw Materials	1134
4.4.	Production	1136
4.5.	Storage and Transportation	1142
4.6.	Testing and Analysis	1142
4.7.	Uses	1144
4.8.	Economic Aspects	1150
4.9.	Toxicology and Occupational Health	1150
4.10.	References	1151

Contents	5	Unsaturated Polyester Resins	1153
	5.1.	Introduction	1153
	5.2.	Raw Materials	1153
	5.3.	Production	1156
	5.4.	Additives	1157
	5.5.	Curing	1159
	5.6.	Types of UP Resins	1159
	5.7.	Testing and Properties	1161
	5.8.	Uses and Economic Aspects	1163
	5.9.	Occupational Health and Environmental Aspects	1165
	5.10.	References	1166
	6	Other Synthetic Resins	1167
	6.1.	Definition	1168
	6.2.	Hydrocarbon Resins	1169
6.3.	Resins by Condensation	1182	
6.4.	Natural and Synthetic Resins—Toxicology and Legislation	1199	
6.5.	References	1202	

4. Polymethacrylates

For poly(methacrylic acid), see Polyacrylamides and Poly(Acrylic Acids). Fundamental aspects of polymerization reactions are treated in Polymerization Processes.

MANFRED STICKLER, Röhm GmbH, Darmstadt, Federal Republic of Germany

THOMA RHEIN, Röhm GmbH, Darmstadt, Federal Republic of Germany

4. Polymethacrylates	619	4.5.1. Molding Compounds	630
4.1. Introduction	619	4.5.1.1. Standard Molding Compounds	630
4.2. Properties	620	4.5.1.2. Heat-Resistant Molding Compounds	631
4.3. Raw Materials	623	4.5.1.3. Impact-Resistant Molding Compounds	632
4.4. Production Processes	624	4.5.1.4. Molding Compounds for Special Optical Uses	633
4.4.1. Bulk Polymerization	625	4.5.2. Semifinished Products	634
4.4.1.1. Casting of Acrylic Glass	625	4.5.2.1. Extruded Acrylic Glass	634
4.4.1.2. Continuous Production of Cast Acrylic Glass	627	4.5.2.2. Cast Acrylic Glass	634
4.4.1.3. Tube Polymerization	627	4.5.3. Binders and Paints	635
4.4.2. Suspension Polymerization	628	4.5.4. Additives for the Petroleum Industry	635
4.4.3. Continuous Polymerization of Molding Compounds	628	4.5.5. Miscellaneous Uses	636
4.4.4. Batchwise Solution Polymerization	629	4.6. Toxicology	636
4.4.5. Emulsion Polymerization	629	4.7. Environmental Aspects	637
4.5. Uses	630	4.8. References	637

4.1. Introduction

Poly(methyl methacrylate) [9011-14-7] (PMMA) has been produced industrially since the early 1930s. The history and development of this polymer are very closely associated with the chemist OTTO RÖHM [1], [2]. In 1932 RÖHM and his collaborator W. BAUER were the first to polymerize methyl methacrylate (MMA) into transparent sheets [3]. Almost parallel to these developments at Röhm & Haas in Germany, corresponding activities were in progress at Rohm & Haas and DuPont in the United States and at ICI in England. A few years later the first thermoplastically processable molding compounds based on PMMA were available.

PMMA occupies an intermediate position between "commodities" and "high-tech polymers" or "engineering plastics"; its market has in the meantime developed greatly. Recent years have been characterized by double-digit growth rates, resulting in high

capacity utilizations and thus an increasing willingness to invest in new production plant equipment. In 1988 the MMA capacities worldwide were ca. 1.5×10^6 t/a (Western Europe 4.7×10^5 t/a, North America 5.1×10^5 t/a, Japan 3.5×10^5 t/a) [4]. About 50 % of this amount is used for further processing into acrylic glass and PMMA molding compounds; the remainder being distributed among dispersions, paints, binders, adhesives, additives, etc.

PMMA is the main representative of this polymer class; polymers and copolymers of higher alkyl methacrylates are of minor economic importance.

4.2. Properties

The properties that make PMMA a highly-prized plastic are its good mechanical strength, its outstanding optical properties (clarity, brilliance, transparency), and its extremely good weather resistance [5]. This favorable profile can be supplemented by the surface modification of semifinished products (e.g., scratch-resistant or antistatic coating), coloring or pigmenting, and treatment with flame retardants to open up a wide variety of potential uses for this polymer (see Chap. 4.5).

Pure PMMA is an amorphous plastic with a high surface gloss, high brilliance, and crystal-clear transparency. It is classified as a hard, rigid, but brittle material. The tensile, compressive, and flexural strengths are considered satisfactory: scratch resistance is also good and can be improved further by the use of special coatings. The most important physical properties of PMMA are summarized in Table 1; a distinction is made between cast PMMA ($M_r > 10^6$) and PMMA extruded from molding compounds ($M_r < 5 \times 10^5$). The properties listed in Table 1 were determined according to the so-called basic value table [6]; further data can be found in the CAMPUS data bank [7]. This data bank also includes information about copolymers of MMA with small proportions of acrylate esters ($< 10\%$ methyl acrylate). Incorporation of acrylate allows the rheological properties of the thermoplastics to be varied within a wide range to satisfy the processing requirements during injection molding and extrusion.

PMMA is resistant to aliphatic hydrocarbons, nonpolar solvents, aqueous alkalis, and aqueous acids. Aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, and other polar solvents attack PMMA, causing it to dissolve or swell. Whereas alcohols and water alone are regarded as nonsolvents, their mixtures may have a solubilizing effect (cosolvency). Detailed information on solvents and precipitating agents for PMMA can be found in [8].

Most physical properties E of polymers depend on the molecular mass. For example, the viscosity of a polymer melt increases continuously with the molecular mass. Some other properties (e.g., glass transition temperature, density, refractive index) show an asymptotic behavior, which can be described by the following equation:

$$E = E_\infty + \frac{k}{M_n} \quad (1)$$

Table 1. Physical properties of PMMA (standard values at 23 °C and 50 % R.H. for Plexiglas GS 233 and Plexiglas XT 7H)

Property	Cast (extruded)*	Test procedure
Density, g/cm ³	1.18	DIN 53 479
Charpy impact strength, kJ/m ²	15	ISO 179/1 D
Izod-test value, kJ/m ²	1.6	ISO 180/1 A
Tensile strength (1/1 test bar 3, $v=5$ mm/min), MPa	80 (72)	DIN 53 455
Elongation at break (1/1 test bar 3, $v=5$ mm/min), %	5.5 (4.5)	DIN 53 455
Flexural strength (standard bar 80×10×4 mm), MPa	115 (105)	DIN 53 452
Long-term tensile strength (1/1 test bar 3, $t=10\,000$ h), MPa	38 (30)	DIN 53 444
Modulus of elasticity (short-term value), MPa	3300	DIN 53 457
Shear modulus (ca. 10 Hz), MPa	1700	DIN 53 445
Ball indentation hardness $H_{961/30}$, MPa	200 (190)	DIN-ISO 2039-1
Degree of transmission (3 mm thickness, illumination D 65, visible region, $\lambda=380-780$ nm), %	92	DIN 5036
Refractive index n_D^{20}	1.491	DIN 53 491
Linear thermal expansion coefficient (0–50 °C), K ⁻¹	70×10^{-6}	DIN 53 752-A
Shrinkage onset temperature, °C	> 80	
Vicat softening point (method B), °C	115 (102)	DIN-ISO 306
Heat distortion temperature (at flexural stress of 1.8 MPa), °C	105 (90)	ISO 75
Water absorption (compared with dry state after 24 h, specimen 50×50×4 mm), mg	30	DIN 53 495

* Extruded from molding compound.

For sufficiently high number-average molecular masses \bar{M}_n , a polymer-specific limiting value E_∞ is accordingly reached (typically at ca. $\bar{M}_n > 50\,000$); the constant k is influenced by the terminal groups of the polymer.

Table 2 summarizes some physical properties of the most important polymethacrylates. The values were obtained at sufficiently high molecular mass (i.e., E_∞), so that the influence of the alcohol residue of the ester group can be recognized.

The glass transition temperatures T_g decrease sharply with the length of the linear, aliphatic side chain. Whereas PMMA, the first member of this homologous series, is a hard, rather rigid material, the polymers with residues larger than n -hexyl are rubber-like. The glass transition temperature decreases up to about poly(dodecyl methacrylate). With longer linear ester residues, side-chain crystallization occurs, which masks the glass transition. Polymers with linear alkyl ester residues always have a lower glass transition temperature than the branched and alicyclic isomers. Large bulky residues considerably restrict the mobility of the polymer main chain, particularly if they are joined directly to the ester group.

When discussing the data in Table 2 it has to be borne in mind that properties of a polymer, in particular the glass transition temperature, also depend on its tacticity. If a tactic polymer is regarded as a terpolymer of isotactic, syndiotactic, and heterotactic triads, then its glass transition temperature can be described by the following linear combination.

$$T_g = x_{ii} T_{g,i} + x_{is} T_{g,h} + x_{ss} T_{g,s} \quad (2)$$

Table 2. Physical properties of the most important polymethacrylates

Polymer	CAS registry no.	ρ (20 °C), g/cm ³	n_D^{20}	T_g , °C	δ , (J/cm ³) ^{1/2}	References
Poly(methyl methacrylate)	[9011-14-7]	1.190	1.490	125	18.6	[9], [12], [13]
Poly(ethyl methacrylate)	[9003-42-3]	1.119	1.485	66	18.3	[9]
Poly(<i>n</i> -propyl methacrylate)	[25609-74-9]	1.085	1.484	35	18.0	[9]
Poly(isopropyl methacrylate)	[26655-94-7]	1.033	1.4728	81		[9], [12]
Poly(<i>n</i> -butyl methacrylate)	[9003-63-8]	1.058	1.483	27	18.0	[9]
Poly(isobutyl methacrylate)	[9011-15-8]	1.045	1.477	53	17.7	[9]
Poly(<i>sec</i> -butyl methacrylate)	[29356-88-5]	1.052	1.480	62		[9], [10], [12]
Poly(<i>tert</i> -butyl methacrylate)	[25189-00-8]	1.022	1.4638	122	17.0	[9], [12]
Poly(<i>n</i> -hexyl methacrylate)	[25087-17-6]	1.007 *	1.481	-5	17.6	[9]
Poly(cyclohexyl methacrylate)	[25768-50-7]	1.100	1.5065	92		[9], [12]
Poly(<i>n</i> -octyl methacrylate)	[25087-18-7]	0.971 *		-20	17.2	[9]
Poly(2-ethylhexyl methacrylate)	[25719-51-1]			-10		[9]
Poly(<i>n</i> -decyl methacrylate)	[29320-53-4]			-70		[10]
Poly(dodecyl methacrylate)	[25719-52-2]	0.929 *	1.4740	-55	16.8	[9]
			**			
Poly(hexadecyl methacrylate)	[25986-80-5]		1.4750			[9]
			**			
Poly(octadecyl methacrylate)	[25639-21-8]			-100	16.0	[9], [13]
Poly(bornyl methacrylate)			1.5059			[9]
Poly(isobornyl methacrylate)	[28854-39-9]	1.060	1.500	110	16.6	[9], [13]
Poly(menthyl methacrylate)	[30847-50-8]	1.010	1.4890	90		[9]
Poly(phenyl methacrylate)	[25189-01-9]	1.210	1.5715	120		[9]
Poly(1-naphthyl methacrylate)	[31547-85-0]		1.6410	75		[9]
Poly(benzyl methacrylate)	[25085-83-0]	1.179	1.5680	54	20.3	[9]
Poly(2-hydroxyethyl methacrylate)	[25249-16-5]		1.5119	55		[9]
Poly(ethylthioethyl methacrylate)	[27273-87-6]		1.5300	-20		[13]
Poly(furfuryl methacrylate)	[29320-19-2]	1.2603	1.5381	60		[9], [12]
Poly(tetrahydrofurfuryl methacrylate)	[25035-85-2]		1.5096	60		[9]
Poly(3,3,5-trimethylcyclohexyl methacrylate)	[75673-26-6]		1.485	79		[9]
Poly(tricyclodecyl methacrylate)				150		[11]
Poly(2,2,3,3-tetrafluoropropyl methacrylate)	[29991-77-3]	1.4934	1.4215	64		[12]

* At 25 °C.

** n_D^{30} .

where $T_{g,i}$, $T_{g,h}$, and $T_{g,s}$ denote the glass transition temperatures of the (imaginary) polymers constructed purely from isotactic, heterotactic, or syndiotactic triads, respectively, and x_{ii} , x_{is} , and x_{ss} denote the associated mole fractions of these triads in the relevant real polymer. In the case of PMMA, the values $T_{g,i}$ =42 °C, $T_{g,h}$ = 139 °C, and $T_{g,s}$ =124 °C were determined by fitting experimental T_g values to x_{ii} , x_{is} , and x_{ss} mole fractions as obtained from NMR analysis [14]; data for other polymethacrylates can be found in the literature [13]. The mole fractions x_{ii} , x_{is} , and x_{ss} depend on the polymerization temperature and the polymerization mechanism (and are possibly influenced also by any solvent used in the polymerization). These relationships have been investigated in detail in the case of PMMA [15].

All the influences on the glass transition temperature described above have not been taken into account in Table 2. Most of the listed T_g values were measured on atactic polymers synthesized by radical polymerization. This explains to some extent the considerable differences that individual authors find in one and the same polymethacrylate. In addition to this, variations also arise due to the use of different methods of measurement of T_g (dilatometry, differential scanning calorimetry) and evaluation procedures (e.g., "midpoint" and "on-set" evaluation in differential scanning calorimetry).

The residual monomer content of the polymers represents a large source of errors in the determination of T_g ; even relatively small proportions can lead to considerable reduction of the glass transition temperature. Methacrylates with bulky side groups (e.g., isopropyl, *tert*-butyl, or cyclohexyl methacrylate) are especially critical because even in the case of a very sharp end polymerization they yield a product that still contains a few percent of residual monomers [16]. The values listed in Table 2 were obtained on reprecipitated, carefully dried material and are considerably higher than previous literature values.

Polymers used as materials for optical application require good transmission behavior; the refractive index and Abbe number are other important parameters. Polymethacrylates exhibit a considerable range of refractive indices; plastics with a particularly low refractive index have been in demand for polymer optic fibers (POF). Fluorinated polymethacrylates are particularly suitable in this connection. A summary of relevant data (T_g , n_D^{20}) is given in [17].

The influence of tacticity on the refractive index and density should also be taken into account, but up to now little information has been available.

4.3. Raw Materials

The starting material for PMMA is the monomer methyl methacrylate (MMA). The most important route to this monomer (as well as to methacrylic acid) is still methanolysis (or hydrolysis) of methacrylamide sulfate. The latter is produced from acetone and hydrogen cyanide via the intermediate acetone cyanohydrin. Alternative synthesis pathways have also been adopted: the C-4 route involves two-stage oxidation of isobutene (or *tert*-butanol) to methacrylic acid and MMA. In the C-3 route propene is reacted with carbon monoxide to give isobutyric acid, from which methacrylic acid is then obtained by oxidative dehydrogenation. The C-2 pathway involves condensation of propanal (or propionic acid) with formaldehyde to methacrolein (or methacrylic acid). Propanal can be obtained from ethylene by hydroformylation.

MMA for polymerization is usually available with a purity of >99.9%; impurities are mainly water, methanol, and traces of acid.

MMA is stabilized for storage or transportation with phenol derivatives (e.g., hydroquinone or hydroquinone monomethyl ether) in amounts of 10–100 ppm; the

stabilizing action of these compounds requires the presence of oxygen. Nitrogen oxides or aromatic nitro compounds can be used in the absence of oxygen. MMA should be stored under exclusion of light and at as low a temperature as possible ($< 10^{\circ}\text{C}$).

To obtain higher methacrylate esters, methacrylic acid is esterified with the relevant alcohols. Longer-chain methacrylate esters are also synthesized by transesterification of MMA.

4.4. Production Processes

Methyl methacrylate can be polymerized by a free radical mechanism [18], [19] or an anionic mechanism [20]–[22]. Anionic polymerization is, however, of no industrial importance because the monomer has to be subjected to extensive purification and polymerization has to be performed at low temperatures. The group transfer polymerization technique (GTP) is mechanistically very similar to anionic polymerization, but is less complicated [23], [24]. It remains to be seen whether this polymerization technique will become industrially important.

Radical polymerization of MMA may be carried out homogeneously (bulk or solution polymerization) or heterogeneously (suspension or emulsion polymerization). It can be initiated with radiation (light, γ -radiation), heat, or radical-forming chemical agents. Spontaneous thermal initiation of MMA polymerization is extremely slow [25] and is therefore of no industrial relevance. Photoinitiation of MMA polymerization can be performed without sensitizers, but photochemically labile compounds are generally added. On exposure to light these compounds form radicals either directly (e.g., azo compounds, disulfides, derivatives of benzoin or acetophenone) or are converted into an excited state and then form radicals after abstracting a hydrogen atom from the monomer or solvent (e.g., derivatives of benzophenone or anthraquinone) [26]–[30]. Initiation of polymerization by γ -rays (e.g., ^{60}Co source) may be of interest if the addition of a thermal initiator is undesirable and a conventional light source cannot be used because the polymerization batch absorbs too strongly (e.g., colored solutions, porous materials such as wood or stone impregnated with monomer [31]).

The polymerization of MMA is most commonly initiated by using thermal radical-forming agents (i.e., initiators). Azo compounds [32], [33] and organic peroxy compounds [33] (diacyl peroxides, dialkyl peroxides, alkyl peresters, peroxy dicarbonates, perketals, alkylhydroperoxides) are often employed. A wide range of initiators is available so that the polymer manufacturer can select an initiator with an appropriate half-life for the relevant polymerization temperature. Redox systems also play an important role in the formation of initiating radicals, particularly in polymerizations in aqueous solution [34].

The polymerization of MMA up to high conversion (particularly in bulk polymerization) is governed by the gel (Trommsdorff) effect [35]. The extremely large increase in the viscosity of the reaction medium during polymerization hinders diffusion of the

polymer radicals considerably. Bimolecular chain termination thus becomes increasingly difficult and the concentration of the growing radicals increases by several orders of magnitude. The result is a sharp rise in the polymerization rate and mean molecular mass [36], which leads to a further increase in the viscosity of the reaction batch. Under these circumstances removal of the heat of polymerization (57.7 kJ/mol for MMA [37]) may become a serious problem or even a potential hazard.

When polymerization is combined with a shaping or forming operation, the considerable decrease in volume associated with polymerization of the monomer may also lead to problems. For the bulk polymerization of MMA shrinkage can be described by the following equation:

$$v = v_M(1 + \epsilon \cdot x) \quad (3)$$

where v_M and v denote the specific volumes of the pure monomer and reaction mixture respectively, x is the degree of conversion, and ϵ is the contraction constant. The dependence of ϵ on the reaction temperature θ (in °C) is given by [38]:

$$\epsilon = -0.2256 - 4.81 \times 10^{-4}\theta - 4.1 \times 10^{-7}\theta^2 \quad (4)$$

At 60 °C, for example, the volume shrinkage of a fully polymerized sample amounts to 25.6 %. Shrinkage decreases with an increase in the size of the alcohol residue of the methacrylate; ϵ calculated on a molar basis remains roughly constant, however.

The method selected for the industrial polymerization of MMA (e.g., bulk, bead, emulsion, or solution polymerization) is generally governed by the form in which the polymer is finally used. Semifinished products (sheets, blocks, rods, tubes) or pellets, beads, dispersions, and solutions may be produced.

4.4.1. Bulk Polymerization

Sheets, rods, and tubes of PMMA can be produced by extrusion of molding powders or by bulk polymerization of monomers or "syrup." The molding powder is obtained by bulk, suspension, emulsion, or solution polymerization.

4.4.1.1. Casting of Acrylic Glass

The conventional casting process is still the most important method for producing high-quality acrylic glass with a mirror-smooth surface (e.g., Plexiglas GS, Perspex, or Vedril). Casting molds are used that consist of two plane-parallel silicate glass plates (e.g., float glass with a typical length, width, and thickness of 3000, 2000, and 8 mm, respectively) which are held apart by a spacer (sealing) and clamped together with metal clamps. The sealing thread runs around the edge of the plates and is usually made of poly(vinyl chloride) or ethylene-vinyl acetate copolymer. It must have sufficient compressibility to allow for the shrinkage occurring during polymerization so that

the acrylic sheet does not become detached from the glass plates. The thickness of the resulting sheets is between a few millimeters and up to ca. 30 cm.

The reaction solution consisting of monomer, initiator, and other additives (e.g., comonomers, cross-linking agents, stabilizers, flame retardants, dyes, or pigments) is introduced into the chamber through a small hole in the sealing. Care must be taken to avoid formation of air bubbles, if necessary the solution should first be evacuated. A monomer-polymer solution (syrup) may be used instead of the monomer solution. This syrup contains 5–20 % PMMA and is obtained by prepolymerization of MMA in a stirred-tank reactor. It is advantageous in that the shrinkage and heat of polymerization in the chamber are lower, and the polymerization time is also reduced. Furthermore, the viscous syrup ensures better dispersion of pigments and prevents leakage from the chamber.

The contents of the sealed cells are polymerized in horizontal wracks mounted in hot-air ovens with a high air circulation rate, in autoclaves using spray water (90–100 °C), or in water tanks (20–60 °C). The residence time may range from a few hours to several days depending on the sheet thickness. Conversion only reaches 80–90 %, however, because the glasslike solidification of the reaction mixture that occurs during polymerization below the glass transition temperature of the pure polymer prevents further reaction (glass effect). Subsequent polymerization at 110–120 °C is therefore necessary to obtain maximum conversion [16], [39]. After cooling to room temperature, the polymer sheet is separated from the glass plates and can be removed. The glass plates are cleaned before being used again.

The conventional casting process described above is labor-intensive and time-consuming; attempts have therefore been made to develop more efficient methods for producing cast PMMA glass. One approach is to pack several plane-parallel glass plates and spacers together. The simplest case is a double cell (three plates with two spacers). More complex constructions have been known for a long time and include a process patented in 1933 in which several glass plates with intermediate seals are stacked in vertical rows. The plates are enclosed on both sides by heatable and coolable metal chambers through which a heat-transfer agent flows, and are held together by a screw press [40], [41]. The heat-transfer agent flowing through the metal chambers allows accurate temperature control. Shrinkage is compensated for by compression of the packet, resulting in strict tolerances of the cast sheets.

In a special variant of this process, the entire apparatus is tightly encapsulated to facilitate degassing of the reaction batch by evacuation. The system is then pressurized to suppress the formation of boiling bubbles caused by local superheating during polymerization. The advantages of this method are the smaller space requirement and reduced workforce. A disadvantage is the fact that the use of metal chambers means that there is less flexibility as regards variation of the sheet sizes. The process is still used on a small scale in Europe (Rostero) and in the United States (Polycast Corp).

In addition to the production of high molecular mass, high-quality, optical acrylic glass, casting polymerization is still occasionally used to produce regular molding compounds and paint resins. Since these products must not have the perfect plane-