

# Chemical Recycling of Polymers. The Case of Poly(methyl methacrylate)

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*Abstract:* - In this contribution, the recycling of poly(methyl methacrylate) is examined using the dissolution/precipitation method, as well as pyrolysis. In the first technique, different solvents/non-solvents were examined at different weight percent amounts and temperatures. The recovery of polymer in every case was greater than 90%. Pyrolysis was carried out in a laboratory fixed bed reactor, using a model polymer as raw material or a commercial product based on PMMA. The liquid fraction constituted mainly of the monomer, together with a number of secondary materials (esters). The potential use of this product as a raw material for the reproduction of poly(methyl methacrylate) by polymerization was investigated using DSC and the results compared with that from virgin monomer. From measurements of the polymerization rate and polymer properties it seems that the existence of other components in the pyrolysis oil fraction leads to lower reaction rates and polymer with inferior properties. Therefore, separation of the monomer is essential.

*Key-Words:* - Polymer recycling, waste minimization, poly(methyl methacrylate), dissolution/precipitation, pyrolysis, polymerization

## 1 Introduction

Recycling of waste plastics has been a topic of interest in the fields of environmental science and technology for some time. The produced amounts of plastic solid wastes continue to increase despite some increasing attempts to reduce, reuse, recycle and recover. This is mainly due to their wide application in the manufacture of packaging for the food industry as well as in other goods of daily life, since they do not have any side effects on the human organism. However, due to the nature of much contaminated plastic wastes they can only be partly recycled into new products. The presently most used way of handling these waste streams is to incinerate them with energy recovery or to use them for land-filling. In the last decade, many environmental regulations have been implemented for a more sustainable recycling oriented society.

The approaches that have been proposed for recycling of waste polymers include [1,2]: *Primary recycling* referring to the "in-plant" recycle of scrap material of controlled history. This process remains the most popular as it ensures simplicity and low cost, dealing however only with the recycling of clean uncontaminated single-type waste. *Mechanical Recycling*, where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion. The main disadvantage is the

deterioration of product properties in every cycle. *Chemical or Feedstock recycling* involves the transformation of polymeric materials by means of heat or chemical agents to yield a variety of products ranging from the starting monomers, to oligomers or mixtures of other hydrocarbon compounds. *Energy recovery* as an effective way to reduce the volume of organic materials by incineration. Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to the health risk from air born toxic substances e.g. dioxins (in the case of chlorine containing polymers). The objective of a plastic management policy, in accordance with the principles of sustainable development, should be not only the reuse of polymeric materials but also the production of raw materials (monomers), from which they could be reproduced, or other secondary valuable products. In this sense, among the techniques proposed for recycling of waste polymers the most challenging method is chemical or feedstock recycling and various technologies have been successfully demonstrated and continue to be developed.

Poly(methyl methacrylate) (PMMA) is a major type of thermoplastic used throughout the world in such applications as transparent all-weather sheets, electrical insulation, bathroom units, automotive

parts, surface coating and ion exchange resins, etc. The plastics made from PMMA are widely used under the commercial trade names PLEXIGLASS or PERSPEX. In Western Europe alone approximately 327 000 tones of PMMA are consumed each year (data of 2003) with an increasing percentage of approximately 4% per year [3]. In contrast with condensation polymers (i.e. poly(ethylene terephthalate) (PET)), addition polymers, like PMMA, can not be easily recycled to monomer by simple chemical methods [4]. Instead, thermochemical recycling techniques like pyrolysis are usually applied. Thus, various processes for the depolymerization of PMMA have been described in literature [5-8]. Furthermore, PMMA thermal pyrolysis results in a close to 97% recovery of the monomer methyl methacrylate (MMA) at relatively low temperatures (400-500°C) [5-7]. However, the possibility of using the liquid pyrolysis product directly for the reproduction of the polymer has not been studied yet in literature.

In the present contribution the chemical recycling of PMMA was examined using two different methods: the traditional method of dissolution/precipitation [9,10] and the more challenging technique of pyrolysis. The first belongs to the mechanical recycling techniques while the second to chemical/feedstock recycling. During the first technique the polymer can be separated and recycled using a solvent/non-solvent system. For this purpose different systems were examined at different weight percent amounts and temperatures. Furthermore, thermal pyrolysis was carried out using either model polymer as raw material or a commercial product (PERSPEX). The experiments were carried out in a laboratory fixed bed reactor. The potential use of the oil produced as a raw material for the reproduction of PMMA by polymerization was investigated using DSC and the results compared with that from virgin monomer. The results for the direct polymer reproduction are not so encouraging.

## 2 Experimental Part

### 2.1 Materials

Model poly(methyl methacrylate) obtained from Aldrich (weight average molecular weight 350 000) and a commercial product made from PMMA (PERSPEX), methyl methacrylate (purity >99%) also from Aldrich. The solvents used (toluene, xylene, n-hexane) were of reagent grade.

### 2.2 Dissolution/precipitation technique

In this approach, model PMMA was used together with the commercial product containing PMMA. Xylene and toluene were used as solvents, while n-hexane as non-solvent. Some other parameters studied include concentration of the polymer, solvent/non-solvent volume ratio and different dissolution temperature below the boiling point for each solvent (140°C for xylene and 110°C for toluene).

The experimental process comprised: the polymer and the solvent were added into a flask equipped with a vertical condenser and a magnetic stirrer. The system was heated for 30 min to the desired temperature. Then, the flask was cooled and the solution of the polymer was properly poured into the non-solvent. The polymer was re-precipitated, washed, filtrated and dried in an oven at 80°C for 10 h. The recycled polymer was obtained in the form of powder or grains.

### 2.3 Pyrolysis

All experiments took place in the Laboratory of Environmental Fuels and Hydrocarbons, situated in CPERI, Thessaloniki, Greece. The reactor was filled with 0.7 g glassbeads and the piston was filled with polymer (1.5 g). The system was always heated in the presence of N<sub>2</sub> (30 mL/min). As soon as the reaction temperatures were achieved, polymer entered the reactor and the experiment started. The time of the experiment was 17 min and the reaction temperature was 450°C. At the end of the experiment, purging (30 min) was performed. Both the experiment (100 mL/min) and purging (30 mL/min) were performed in the presence of N<sub>2</sub>. Details on the procedure can be found in references [11,12].

The liquid products were collected in a liquid bath (-17 °C) and quantitatively measured in a pre-weighted glass receiver. The gaseous products were collected and measured by water displacement. The liquid samples were analysed by GC/MS analysis in a HP 5989 MS ENGINE. Gaseous products were analysed in a HP 6890 GC, equipped with four columns and two detectors (TCD and FID). The chromatograph was standardized with gases at known concentrations as standard mixtures.

### 2.4 Re-polymerization of the pyrolysis oil

Azo-bisobutyronitrile (AIBN) was used as an initiator of the free radical polymerization of MMA. Solutions of either pure MMA (monomer), or the liquid fraction from pyrolysis with initiator were prepared at a concentration of AIBN 0.03 M.

Polymerization was investigated using the DSC, Pyris 1 (from Perkin-Elmer) equipped with the Pyris software for windows. Indium was used for the enthalpy and temperature calibration of the instrument. Polymerizations were carried out at different temperatures. The reaction temperature was recorded and maintained constant (within  $\pm 0.01$  °C) during the whole conversion range. The samples were weighted (approximately 10 mg) sealed and placed into the appropriate position of the instrument. The reaction exotherm (in normalized values, W/g) at a constant temperature was recorded as a function of time. The rate of heat release ( $d(\Delta H)/dt$ ) measured by the DSC was directly converted into the overall reaction rate ( $dx/dt$ ) using the following formula:

$$\frac{dx}{dt} = \frac{1}{\Delta H_T} \frac{d(\Delta H)}{dt}$$

where  $\Delta H_T$  denotes the total reaction enthalpy. The polymerization enthalpy was calculated by integrating the area between the DSC thermograms and the baseline established by extrapolation from the trace produced after complete polymerization (no change in the heat produced during the reaction).

### 2.5 Measurements

The glass transition temperature,  $T_g$ , of the model PMMA, the commercial sample as well as the samples obtained after the dissolution/precipitation technique together with the polymers produced after the repolymerization procedure was measured using the Pyris-1 DSC from Perkin Elmer. Samples of approximately 10 mg were introduced into the appropriate position of the instrument and the heat released was recorded at a temperature interval 20 to 150°C and a scan rate of 20°C/min.  $T_g$  was calculated using the well-known procedure at the point where a change in the slope of the curve was observed.

In order to identify the commercial product as well as the product obtained after the dissolution/precipitation technique the IR spectra of the samples was recorded. The instrument used was an FTIR spectrometer of Perkin-Elmer, Spectrum One. The resolution of the equipment was 4  $\text{cm}^{-1}$ . The recorded wavenumber range was from 450 to 4000  $\text{cm}^{-1}$  and 16 spectra were averaged to reduce the noise. A commercial software Spectrum v5.0.1 (Perkin Elmer LLC 1500F2429) was used to process and calculate all the data from the spectra.

## 3 Results and Discussion

### 3.1 Recycling of PMMA by the dissolution/precipitation technique

Two solvent/nonsolvent systems and three dissolution temperatures were investigated. The effect of temperature, polymer percentage, as well as solvent/nonsolvent used on the % recovery of PMMA from the model polymer and the commercial product (PERSPEX) appears in Table 1. As it can be seen polymer recovery is favored by temperature, less amount of polymer and use of toluene instead of xylene as a solvent. The recoveries obtained from the commercial product were similar or higher than that of the model polymer.

Table 1. PMMA recovery by the dissolution/precipitation technique

Solvent/ non-solvent	T (°C)	Polymer w/v	Non-solv/ solv (v/v)	Recovery
Toluene/ n-hexane	22	Model 20%	3:1	36%
Toluene/ n-hexane	50	Model 20%	3:1	75%
Toluene/ n-hexane	70	Model 20%	3:1	90%
Toluene/ n-hexane	22	Model 10%	3:1	43%
Toluene/ n-hexane	50	Model 10%	3:1	90%
Toluene/ n-hexane	22	Model 10%	2:1	47%
Toluene/ n-hexane	50	Model 10%	2:1	98%
Xylene/ n-hexane	22	Model 10%	3:1	18%
Xylene/ n-hexane	50	Model 10%	3:1	52%
Toluene/ n-hexane	22	PERSPEX 10%	3:1	78%
Toluene/ n-hexane	50	PERSPEX 10%	3:1	90%
Toluene/ n-hexane	22	PERSPEX 10%	2:1	82%
Toluene/ n-hexane	50	PERSPEX 10%	2:1	95%
Xylene/ n-hexane	22	PERSPEX 10%	3:1	28%
Xylene/ n-hexane	50	PERSPEX 10%	3:1	99%

Comparing the FT-IR spectra of the solid obtained from commercial samples with that of model PMMA identified the polymer recovered with this technique. The interpretation of spectra showed that the product of recycling was PMMA. Indicative spectra are presented in Figure 1.

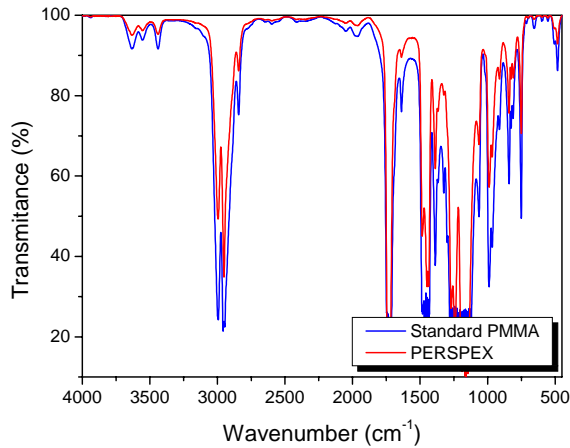
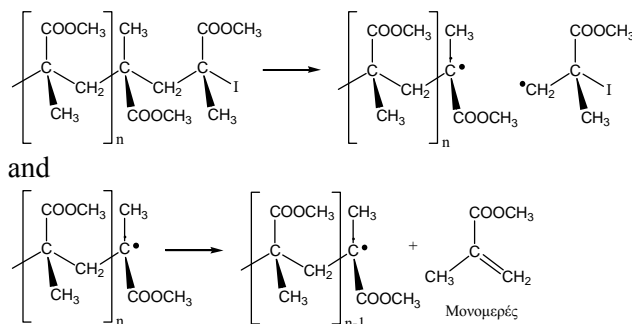


Fig. 1 FT-IR spectra of model PMMA and a commercial product (PERSPEX) containing that polymer

### 3.2 Recycling of PMMA by pyrolysis

Thermal cracking or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen (usually in a nitrogen atmosphere). During pyrolysis at increased temperatures, depending on polymer type, either end-chain, or random scission of the macromolecules occurs. In the first case (occurring in poly(methyl methacrylate)) the monomer can be produced in a large amount, while in the second (polyethylene) the amount of monomer produced is very low. In some other polymers, like polystyrene, degradation is in the middle, meaning that both end-chain and random scission occur simultaneously.

The mechanism of macromolecular degradation (end-chain scission) in the case of PMMA appears next:



Results on the pyrolysis conditions and product yield appear in Table 2. It can be seen that the liquid product in both polymers is very high, approximately 99%.

Table 2. Pyrolysis temperature and product yield from the thermal pyrolysis of model PMMA and a commercial product containing that polymer.

Polymer	Model PMMA	PERSPEX
Temperature (°C)	450	450
Gas (wt-%)	0.6	0.8
Liquid (wt-%)	99.3	98.7
Residue (wt-%)	0.1	0.5
Total monomer recovery	98.3	95.4

Furthermore, the composition of gaseous and liquid products appears in Tables 3 and 4, respectively.

Table 3. Composition (%) of the pyrolysis gaseous fraction of the model PMMA and the commercial product containing PMMA

Gaseous Products	Polymer	
	Model PMMA	PERSPEX
H <sub>2</sub>	0.0	0.0
CO <sub>2</sub>	52.4	50.2
CO	25.8	29.5
CH <sub>4</sub>	17.0	10.0
C <sub>2</sub> H <sub>6</sub>	0.0	0.0
C <sub>2</sub> H <sub>4</sub>	0.8	1.2
C <sub>3</sub> H <sub>8</sub>	0.0	0.0
C <sub>3</sub> H <sub>6</sub>	1.7	3.7
C <sub>4</sub>	1.2	4.4
nC <sub>5</sub>	0.0	0.0
IC <sub>5</sub>	1.1	1.0
<i>Total</i>	<i>100.0</i>	<i>100.0</i>

It was observed (Table 3) that the gas composition of both samples was approximately the same with large amounts of CO<sub>2</sub> and CO due to the existence of oxygen in the macromolecular chain together with methane. Some C<sub>3</sub> and C<sub>4</sub> hydrocarbons are produced but in small amounts. It should be noticed here that the weight percent amount of the gaseous product from both polymers is very low (Table 2).

Table 4. Organic compounds identified in the liquid fraction of the thermal pyrolysis of model PMMA and the commercial product containing PMMA (%)

Liquid products	Polymer	
	Model PMMA	PERSPEX
Methyl methacrylate <b>(monomer)</b>	99.0	96.7
Propanoic acid, methyl ester	0.1	0.5
Propanoic acid, 2-methyl-, methyl ester	0.1	0.7
Propanoic acid, 2,2- dimethyl-, methyl ester	0.2	0.4
Cyclohexanecarboxylic acid, ethenyl ester	0.1	0.2
Cyclohexane, 1-methyl-2- pentyl-	0.1	0.2
1,3-Pentadiene, 2,4- dimethyl-	0.0	0.3
Butanedioic acid, methylene- dimethyl ester	0.2	0.3
1,4-Cyclohexanedicarboxylic acid, dimethyl ester	0.1	0.4
Cyclohexanone, 2,5- dimethyl-2-(1-methyl)	0.0	0.2
Other compounds	0.1	0.1

From Table 4 it was observed that the liquid fraction mostly consists of the monomer MMA in a large amount (>96%) with a small percentage of some other ester. Thus literature results were verified [13].

### 3.3 Re-polymerization of the oil fraction

This step includes the main contribution of the present contribution where the possibility of using directly the liquid fraction received from pyrolysis for the reproduction of the polymer is investigated.

In Fig. 2 polymerization reaction rate of the oil fraction as a function of time at different polymerization temperatures are presented. It can be noticed that polymerization happens at all temperatures with higher rates at elevated temperatures. In order to check the quality of the liquid product, additional experiments were carried out but using fresh methyl methacrylate monomer this time. Indicative experimental data of the reaction rate versus time at 80°C appear in Figure 3. It can be seen that the product of thermal cracking results in a profile resembling that of the pure MMA monomer, though not exactly the same. It seems that

although the percentage of monomer is high in the oil fraction, the existence of other esters acts rather as an inhibitor or retarder for the reaction. This result was verified by measuring the glass transition temperature of the polymer produced at different temperatures. Results appear in Table 5. It was noticed that at all temperatures the polymer produced from the pyrolysis liquid fraction exhibited a Tg lower than that obtained from fresh monomer by approximately 20°C. It is known that polymers with lower average molecular weight show also lower values of Tg. Thus, the polymer produced probably has a lower average molecular weight due to the existence of the other components in the liquid fraction and their retarding action in polymerization.

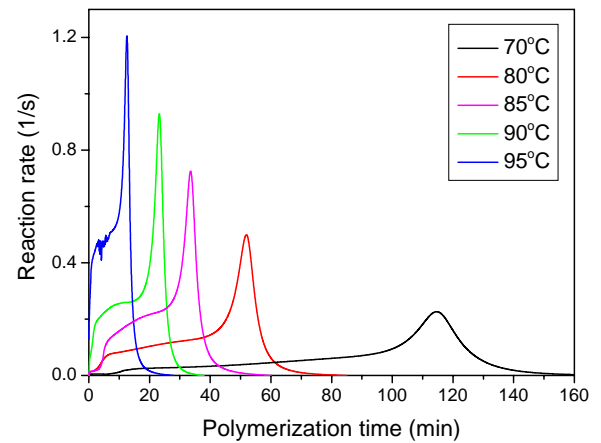


Fig. 2. Polymerization rate versus time of pyrolysis oil fraction at different temperatures. Initiator: AIBN 0.03M.

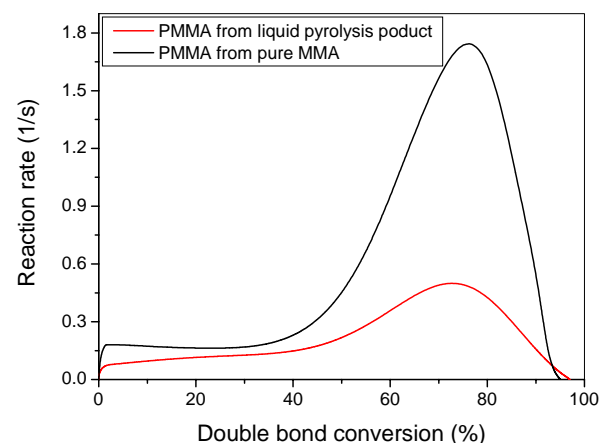


Fig. 3. Polymerization rate versus double bond conversion of pyrolysis oil fraction compared to polymerization of fresh methyl methacrylate monomer. Initiator: AIBN 0.03M, temperature 80°C.

The maximum double bond conversion obtained in both cases was approximately the same (Table 5). Therefore, the possibility of using directly the oil product from pyrolysis for the reproduction of PMMA is under question.

Table 5. Maximum double bond conversion and glass transition temperature of the polymer obtained at different polymerization temperatures either from pure monomer MMA (PMMA PM) or from the liquid pyrolysis product (PMMA LPP)

Polymer. Temper. (°C)	$X_{max}(\%)$		$T_g$ (°C)	
	PMMA PM	PMMA LPP	PMMA PM	PMMA LPP
70	93	94	106	88
80	95	97	106	87
85	96	98	105	87
90	97	98	104	85
95	98	98	103	84

#### 4 Conclusions

In this contribution, the chemical recycling of poly(methyl methacrylate) was examined by both a dissolution/precipitation technique and pyrolysis. The first leads to high recovery of polymer with the disadvantage of using large amounts of organic solvents. Pyrolysis seems to be the most promising technique resulting in an oil fraction with a great percentage of methyl methacrylate monomer. The possibility of using the liquid fraction for the reproduction of PMMA was investigated. From the results obtained from DSC measurements on polymerization rate it is concluded that the liquid fraction can be polymerized using the appropriate initiator but with a lower rate compared to fresh monomer. Furthermore, the polymer produced has inferior properties (lower glass transition temperature and average molecular weight) compared to the polymer produced from pure MMA. Thus, even small amounts of admixtures present in the liquid fraction act as retarders in the re-polymerization reaction.

#### Acknowledgements

This work was funded by the E.K.T. / E.I.I.E.A.E.K. II in the framework of the research program PYTHAGORAS II, Metro 2.6.

I would like also to thank Mrs. E. Antonakou for carrying out the two pyrolysis experiments and Dr. A. Lappas from CPERI.

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