Influence of 2,4,6-trimethylphenol on the yield of synthesis and properties of poly(phenylene oxide)

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Abstract: The influence of 2,4,6-trimethylphenol (2,4,6-TMP) — a by-product of 2,6-dimethylphenol (2,6-DMP) preparation — on the process of poly(phenylene oxide) (PPO) synthesis is presented. Synthesis of the polymer was carried out with solution and precipitation method. 2,4,6-TMP was used in the amount up to 2.2 wt % in both processes. The molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and the dispersity (*Đ*) of the polymers obtained were determined by gel permeation chromatography (GPC). Thermal properties using (DSC, TGA), and the mass melt flow rate (*MFR*) were also determined. In contrast to the precipitation method, it was found that 2,4,6-TMP had a strong effect on properties of PPO obtained by solution polymerization. Addition of 2,4,6-TMP to the monomer solution caused a decrease in molecular weight of polymers. A change of *Đ* value and thermal properties were also noticed. An addition of 2,4,6-TMP up to 2.2 wt % to the reaction in the solution polymerization caused increase in *MFR*, whereas alcohol used in the precipitation polymerization of 2,6-DMP strongly determined properties of the polymer obtained.

Keywords: poly(phenylene oxide), poly(2,6-dimethyl-1,4-phenylene ether), oxidative polymerization, 2,6-dimethylphenol, 2,4,6-trimethylphenol.

Wpływ 2,4,6-trimetylofenolu na wydajność syntezy i właściwości poli(tlenku fenylenu)

Streszczenie: W artykule zaprezentowano otrzymywanie poli(tlenku fenylenu) (PPO) metodą polimeryzacji utleniającej 2,6-dimetylofenolu (2,6-DMP) z dodatkiem 2,4,6-trimetylofenolu (2,4,6-TMP). 2,4,6-TMP jest jednym z głównych zanieczyszczeń 2,6-DMP i powstaje podczas jego syntezy, jako wynik dalszego metylowania. W artykule przedstawiono wpływ 2,4,6-TMP (w ilości do 2,2 % mas.) na właściwości PPO i wydajność syntezy prowadzonej dwiema metodami: rozpuszczalnikową (w toluenie) i strąceniową (w mieszaninie 64,8 % obj. toluenu i 35,2 % obj. etanolu). Ciężary cząsteczkowe ($\overline{M}_n$ and $\overline{M}_w$) i współczynnik polidyspersyjności (*Đ*) otrzymanych polimerów wyznaczano za pomocą chromatografii żelowej (GPC). Właściwości termiczne PPO badano metodami analizy termicznej (TGA i DSC), a ponadto wyznaczano również masowy wskaźnik szybkości płynięcia (*MFR*). Wpływ obecności 2,4,6-TMP na produkt reakcji był znacznie większy w przypadku zastosowania polimeryzacji rozpuszczalnikowej niż w przypadku metody strąceniowej. Zaobserwowano wówczas zmniejszenie wydajności z 90 do 85 %, zmniejszenie $\overline{M}_w$ z $7{,}04 \cdot 10^4$ do $2{,}07 \cdot 10^4$, czemu towarzyszył wzrost wartości *MFR* od nieoznaczalnie małego do 1,51 g/10 min oraz wzrost wartości *Đ* z 2,4 do 4,5. W przypadku metody strąceniowej uzyskano wydajność wahającą się w granicach 91,3—94,2 %, a ze wzrostem zawartości 2,4,6-TMP $\overline{M}_w$ polimeru zmniejszał się z $4{,}69 \cdot 10^4$ do $3{,}76 \cdot 10^4$, wartość *Đ* wzrastała z 2,3 do 3,7, a *MFR* z 0,19 do 0,63.

Słowa kluczowe: poli(tlenek fenylenu), polieter(2,6-dimetylo-1,4-fenylenowy), polimeryzacja utleniająca, 2,6-dimetylofenol, 2,4,6-trimetylofenol.

Poly(2,6-dimethyl-1,4-phenylene ether) also known as poly(phenylene oxide) (PPO) is a commercially important thermoplastic material [1, 2]. The polymer shows excellent mechanical properties at elevated temperature, a good resistance to moisture and to wide range of chemicals [3, 4]. Due to its high glass transition temperature ($T_g \approx 210$ °C) [5], it is often blended with other thermoplastics, like polystyrene [3, 6, 7] or polyamide [8, 9], what reduces the T_g value and makes processing easier. PPO blends are widely used in many industrial applications, for instance in the automotive industry [10], computer and television casings and keyboard frames [11].

PPO was first time synthesized in 1959 by Hay et al. [12] by the oxidative polymerization of 2,6-dimethylphenol (2,6-DMP). The reaction shown in Scheme A, was

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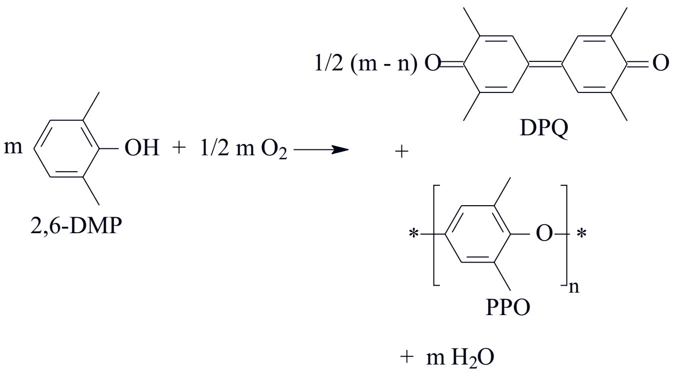


Scheme A

catalyzed by copper-amine complex in the atmosphere of oxygen. Two coupling reactions run during the reaction: C-O coupling leads to PPO formation while C-C coupling leads to the formation of undesirable by-products: 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone) (DPQ) and water [1, 3, 4, 12, 13].

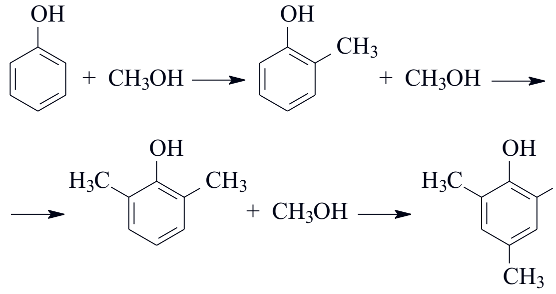
At present there are several methods of PPO preparation, such as microwave assisted polymerization [14], suspension polymerization [15] or reaction with immobilized catalysts [16]. Unfortunately those methods have no technological importance. There are only two technological methods of the oxidative polymerization of 2,6-dimethylphenol:

— solution polymerization (both monomer and polymer are soluble in the solvent used as a polymerization medium),

— precipitation polymerization (monomer and oligomers are soluble in the solvent used as a polymerization medium but the polymer precipitates during the process).

The monomer used in this reaction (2,6-DMP) is produced in chemical reaction, presented in Scheme B, of phenol and methyl alcohol in the presence of a metal catalyst [17—21].

During the methylation process not only 2,6-DMP but also other substances are received, such as: *para* and *orto* cresols; isomeric 2,3-, 2,4-, 2,5-dimethylphenols and others [18, 19, 22]. The major by-products of this reaction are *o*-cresol and 2,4,6-trimethylphenol (2,4,6-TMP), also known as a mesitol [17, 20], both are present in 2,6-DMP as impurities.



Scheme B

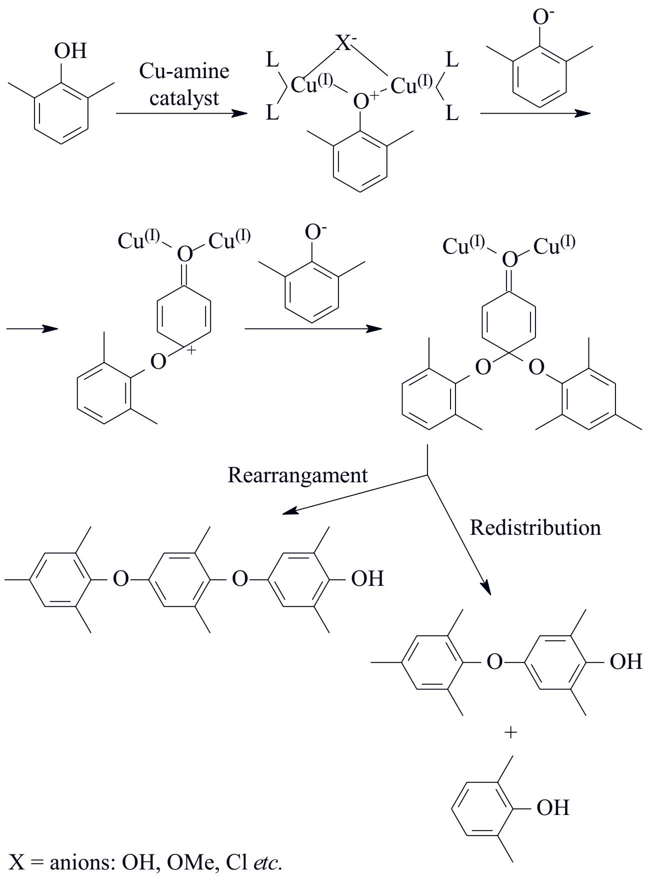
The impurities present in 2,6-DMP may have different effects on these processes because of different molecular weight regulation mechanisms:

— in solution polymerization polymer chain may attain big length, only polymerization time and presence of chain ending impurities limit the polymer chain size,

— in precipitation polymerization polymer chain length is limited by solubility in the polymerization medium, long chain polymer becomes insoluble in the solvent and precipitates.

Fine purification of 2,6-xylenol from *o*-cresol and 2,4,6-TMP is expensive because of their close boiling points (191, 203 and 220 °C for *o*-cresol, 2,6-xylenol and 2,4,6-TMP, respectively) so it is very important to indicate a point when impurities included in raw material start to disturb polymerization process. Oxidation route of 2,4,6-TMP is under investigation, because it can lead to 4-hydroxy-3,5-dimethylbenzaldehyde, which is a valuable intermediate product for drugs preparation [23]. But such investigations give no knowledge about the impact of 2,4,6-TMP presence in the raw material on PPO preparation process with methods of technological importance.

In Scheme C a mechanism based on Dutch researchers proposition [24] of C-O coupling including presence of 2,4,6-TMP was presented. After association of 2,4,6-TMP



X = anions: OH, OMe, Cl *etc.*

Scheme C

anion to the cation generated in the intermediate dimer structure, C-O coupling takes place and a quinone-ketal molecule is formed. In the next steps polymer formation is followed by repeated rearrangement and redistribution reactions. 2,4,6-TMP decreased reaction rate of the oxidative coupling polymerization by coordination to the copper atoms and creating an active complex which is oxidized to 3,5-dimethyl-4-hydroxybenzaldehyde mentioned earlier. Secondly, if 2,4,6-TMP anion is connected to the *para* position of the catalytically active oligomeric quinone-ketal moiety, the following reactions are slowed down due to the fact that the methyl group in the *para* position blocks one of the rearrangement pathways.

In this paper, the effect of 2,4,6-TMP on the yield of PPO synthesis and polymer properties was investigated. The catalysts based on copper(II) bromide-dibutylamine ($CuBr_2$-DBA) for solution polymerization and copper(II) chloride-morpholine ($CuCl_2$-Mor) for precipitation polymerization were used. Use of different catalysts for solution and precipitation polymerization was necessary because of the work idea which was effective control of PPO molecular weight using a proper amount of 2,4,6-TMP, according to the polymerization method. On the contrary to $CuBr_2$-DBA the catalyst based on $CuCl_2$-Mor is less active in the PPO polymerization in pure toluene. The results obtained (reaction yield and physicochemical properties of the polymer) were compared with the results received for PPO synthesized without 2,4,6-TMP.

EXPERIMENTAL PART

Materials

All reagents were of analytical grade. The 2,6-dimethylphenol (2,6-DMP, purity > 99 %, Sigma Aldrich), 2,4,6-trimethylphenol (2,4,6-TMP, ABCR), copper(II) bromide (Sigma Aldrich), copper(II) chloride (POCh), dibutylamine (Fluka), morpholine (Sigma Aldrich) and chloroform (Chempur) were used as received. Toluene (Chempur) and ethanol (Vevex) were dried on molecular sieves (3A) prior to use.

Synthesis of PPO

The solution polymerization

The process of solution oxidative polymerization of 2,6-DMP to poly(2,6-dimethyl-1,4-phenylene oxide) was carried out at 25 °C in the oxygen atmosphere. The solution containing 0.2 mol of 2,6-DMP in 70 cm^3 of toluene and 2,4,6-TMP up to 2.2 wt % of the raw material was dosed for 90 min to a stirred mixture of the catalytic system based on 0.8 mmol of copper(II) bromide and 66.5 mmol of dibutylamine in 70 cm^3 of toluene. After 90 min, the process was stopped by adding 10 cm^3 of acetic acid. The product was precipitated with ethanol, filtered, washed by the same solvent and dried.

The precipitation polymerization

The process of oxidative polymerization of 2,6-DMP was carried out at 25 °C in the oxygen atmosphere. The solution containing 0.2 mol of 2,6-DMP in the mixture of 48.6 cm^3 of toluene and 26.4 cm^3 of ethanol and 2,4,6-TMP up to 2.2 wt % was dosed for 90 min to a stirred mixture of the catalytic system based on 0.8 mmol of copper(II) chloride and 66.5 mmol of morpholine in the mixture of 48.6 cm^3 of toluene and 26.4 cm^3 of ethanol. Ethanol was used as the non-solvent for poly(phenylene oxide). After 90 min, the process was stopped by adding 10 cm^3 of acetic acid. The polymer was filtered, washed by ethanol and dried.

Methods of testing

The weight-average molecular weight ($\overline{M}_w$) of PPO was measured by GPC, using an apparatus of LabAlliance. The apparatus was equipped with a refractometric detector and a Jordi Gel DVB Mixed Bed (250 mm × 10 mm) column. The polystyrene was used as a standard calibration sample. The mass melt flow rate (*MFR*) measurements were carried out using IIRT plastometer according to the standard PN-EN ISO 1133:2006. Thermogravimetric analysis (TGA) of polymer was performed using a TGA/SDTA 851e Mettler Toledo thermogravimetric analyzer under the nitrogen atmosphere. Samples (20 mg) were placed in aluminum oxide pans without lids. Heating scans were carried out from 25 to 700 °C at the heating rate of 10 °C/min. The onset of the decomposition temperature and the total weight loss were determined. Differential scanning calorimetry (DSC) measurements were performed using a DSC 822e differential scanning calorimeter (Mettler Toledo). The instrument was calibrated with high-purity indium as a standard. Samples of about 5 mg were weighed into aluminum pans. The samples was heated at the rate of 10 °C/min from 30 to 300 °C, cooled down to 30 °C, and heated again. The nitrogen flow was 50 cm^3/min.

RESULTS AND DISCUSSION

Yield and molecular weight of PPO

In our work we were trying to obtain an efficient catalytic system for the oxidative polymerization of 2,6-DMP. Unfortunately, the complex used cannot be used exchangeably in both polymerization methods. The best results in the precipitation polymerization gave the catalytic system based on copper(II) chloride and morpholine, whilst in the solution polymerization copper(II) bromide-dibuthylamine complex. Probably, the main reasons of this situation are the type of the counter anions in the copper halide and chemical interaction of the amine ligand with the solvent used or solvents mixture, according to the solvation phenomena.

The results of the yield of the oxidative polymerization of the 2,6-DMP with various 2,4,6-TMP content by precipitation or solution polymerization are presented in Table 1. In comparison to the solution polymerization, the addition of 2,4,6-TMP to the monomer solution does not results in definite decrease in the yield of PPO synthesis obtained in the precipitation method. It is caused by presence of alcohol in the reaction environment. Alcohol limits the weight of the growing polymer chains acting as a precipitation agent.

Table 1. Effect of the 2,4,6-TMP content on the yield, weight-average molecular weight ($\overline{M}_w$), number-average molecular weight ($\overline{M}_n$) and dispersity (Đ) of PPO

Polymerization method	Sample symbol	2,4,6-TMP content wt %	Yield of PPO synthesis, %	$\overline{M}_w\cdot10^{-4}$	$\overline{M}_n\cdot10^{-4}$	Đ
Solution polymerization	P-1	0	90.4	7.04	2.91	2.4
	P-2	0.3	91.2	5.83	2.39	2.4
	P-3	0.6	92.7	5.92	1.98	3.0
	P-4	1.1	89.7	4.62	1.49	3.1
	P-5	1.7	86.8	3.61	0.975	3.7
	P-6	2.2	85.2	2.07	0.461	4.5
Precipitation polymerization	P-7	0	93.5	4.69	2.06	2.3
	P-8	0.3	94.2	4.49	1.32	3.4
	P-9	0.6	93.9	4.21	1.21	3,5
	P-10	1.1	91.3	3.92	1.19	3.3
	P-11	2.2	94.7	3.76	1.03	3.7

The addition of 2,4,6-TMP to the monomer solution in the solution method results in a decrease in the polymer yield from 90.4 % for P-1 sample obtained without TMP, to 85.2 % for P-6 sample (2.2 wt % of 2,4,6-TMP).

As it was shown in Table 1, the molecular weight of the polymer obtained by solution polymerization (P-1 sample, $\overline{M}_w = 7.04 \cdot 10^4$) is higher than of the polymer obtained by the precipitation method (P-7 sample, $\overline{M}_w = 4.69 \cdot 10^4$). The strongest 2,4,6-TMP impact on the polymer molecular weight was found in the solution method. The $\overline{M}_w$ value of PPO decreased significantly from $7.04 \cdot 10^4$ (for P-1) to $2.07 \cdot 10^4$ (for P-6) when 2,4,6-TMP was added. It was caused by termination or slow down effect of 2,4,6-TMP in the oxidative polymerization. Thanks to the reactive site blocked by the methyl group present at *para*-position, 2,4,6-TMP may be used as a molecular weight regulator in the PPO synthesis with the solution method.

Similar but much weaker correlation was noticed for PPO prepared with the precipitation method. With increasing 2,4,6-TMP content up to 2.2 wt %, the decrease in the $\overline{M}_w$ from $4.69 \cdot 10^4$ (for P-7) to $3.76 \cdot 10^4$ (for P-11) was observed. The change of $\overline{M}_w$ is too small to treat 2,4,6-TMP as a molecular weight regulator in PPO synthesis with the precipitation method.

PPO prepared by solution polymerization of 2,6-DMP is characterized by dispersity in the range from 2.4 (for P-1 sample, no 2,4,6-TMP) to 4.5 (for P-6 sample, 2.2 wt % of 2,4,6-TMP). With increasing content of 2,4,6-TMP (to 2.2 wt %) an increase in dispersity to 4.5 (for P-6) was observed. PPO obtained in the precipitation polymerization is characterized with the disperisty equal to 2.3 (for P-7 sample). With increasing 2,4,6-TMP content, an increase in the molecular weight dispersity from 3.4 (for P-8) to 3.7 (for P-11) was observed.

The curves of the molecular weight dispersity of the PPO polymers prepared by solution and precipitation polymerizations are presented in Figs 1 and 2. Analyzing the molecular weight dispersity curves we can see that in general monomodal molecular weight dispersities were obtained. Addition of 2,4,6-TMP to the monomer solution changes the polymer dispersity, especially of PPO obtained with the solution method. There were no molecular weight dispersity curves changes for polymers prepared with the precipitation method at ≥ 0.3 wt % of 2,4,6-TMP content. In the solution method 2,4,6-TMP addition, especially above 1.1 wt %, widens the molecular weight dis-

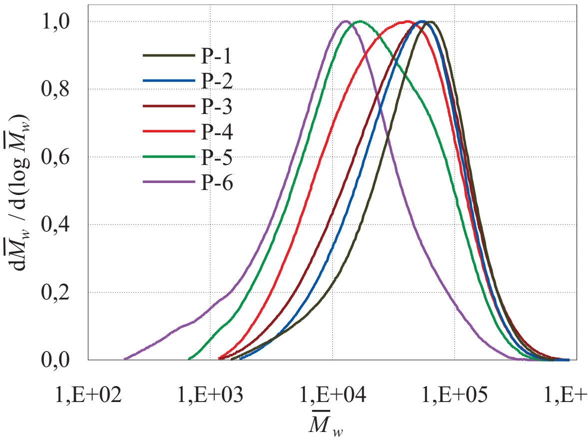


Fig. 1. Differential curves of the molecular weight dispersity of the PPO samples obtained in solution polymerization in the presence of 2,4,6-TMP (samples denotations as in Table 1)

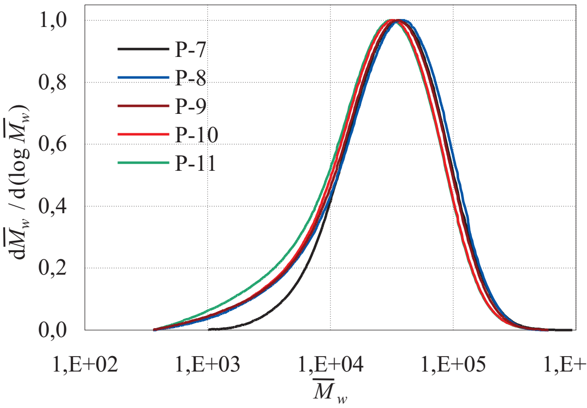


Fig. 2. Differential curves of the molecular weight dispersity of PPO samples obtained in precipitation polymerization in the presence of 2,4,6-TMP (samples denotations as in Table 1)

persity and shifts down the molecular weights of the polymers prepared. Above this 2,4,6-TMP content, the lower molecular weights were determined. It was probably caused by 2,4,6-TMP end groups terminating the polymer chains and so influencing the polymer chain length.

MFR of PPO

MFR is a standard parameter from the technological point of view devoted to polymer characterization. Measurements are fast and allow estimating flow properties of the polymer. The influence of 2,4,6-TMP present in the monomer solution on the value of *MFR* of PPO is presented in Table 2. As it was shown in Table 1, 2,4,6-TMP plays an important role as a molecular weight regulator in the oxidative polymerization of 2,6-DMP. 2,4,6-TMP reduces the molecular weight of PPO obtained with the solution method. With increasing 2,4,6-TMP content, the value of the *MFR* increases, what means that polymer has lower $\overline{M}_w$. The lower change of *MFR* was observed for polymers obtained with the precipitation method, where PPO non-solvent with higher polarity caused polymer precipitation and resulted in limiting the impact on the properties of products.

Table 2. Influence of 2,4,6-TMP content on *MFR* of PPO

Polymerization method	Sample symbol	2,4,6-TMP content, wt %	*MFR* g/10 min
Solution polymerization	P-1	0	DF[a]
	P-2	0.3	DF[a]
	P-3	0.6	0.22
	P-4	1.1	0.45
	P-5	1.7	0.81
	P-6	2.2	1.51
Precipitation polymerization	P-7	0	0.19
	P-8	0.3	0.21
	P-9	0.6	0.35
	P-10	1.1	0.60
	P-11	2.2	0.63

[a] DF — does not flow.

Thermal properties of PPO

PPO is thermally stable polymer with the glass transition temperature (T_g) in the range between 210 and 220 °C. The most critical for thermal degradation of PPO are C_{ar}-C_{al}, C_{ar}-O and C-H bonds. The C_{ar}-H and C_{ar}-C_{ar} bonds have higher bond energy so they are less liable to scission. As it was presented in Table 3, regardless of the polymerization method, PPO obtained without 2,4,6-TMP shows high value of T_g about 220 °C.

2,4,6-TMP present in the reaction environment caused a decrease in T_g of the polymer. The significant T_g decrease was observed for polymers obtained with the solution method. DSC thermograms of polymers obtained with both methods with or without 2,4,6-TMP are presented in Fig. 3. The lack of both the crystallization exotherm

Table 3. Effect of 2,4,6-TMP content on thermal properties of PPO

Polymerization method	Sample symbol	2,4,6-TMP content wt %	T_g, °C	T_{onset}, °C	Weight loss, %
Solution polymerization	P-1	0	220	442.5	67.6
	P-2	0.3	218	442.0	66.1
	P-3	0.6	216	441.0	65.9
	P-4	1.1	215	442.8	67.8
	P-5	1.7	210	441.0	65.8
	P-6	2.2	205	440.2	67.0
Precipitation polymerization	P-7	0	220	437.0	67.0
	P-8	0.3	219	438.2	70.7
	P-9	0.6	219	437.6	70.2
	P-10	1.1	218	437.0	69.7
	P-11	2.2	217	437.0	70.8

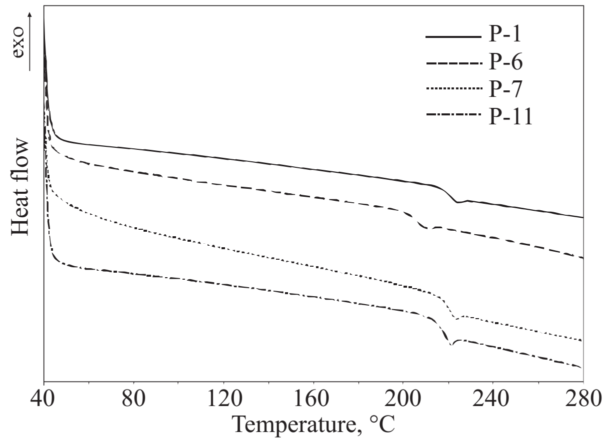


Fig. 3. DSC curves of PPO samples obtained by solution (P-1 and P-6 samples) or precipitation polymerization (P-7 and P-11 samples)

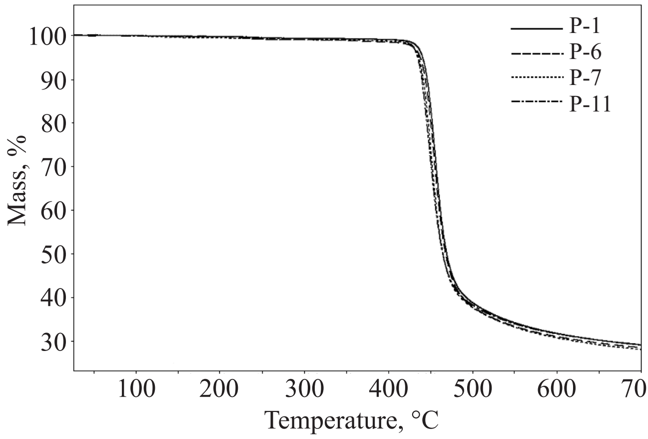


Fig. 4. TGA curves of PPO samples obtained by solution (P-1 and P-6) or precipitation polymerization (P-7 and P-11)

peak above T_g and the melting endotherm peak indicates that the polymer is amorphous.

The onset temperature (T_{onset}) of the polymer decomposition was close to 440 °C and the weight loss differences were very small (Fig. 4). Polymer prepared with the solution method is more resistant to thermal decomposition than the polymer obtained with the precipitation method due to higher molecular weight.

CONCLUSIONS

The results presented in this paper showed that 2,4,6-TMP strongly influences on the preparation and physicochemical and thermal properties of PPO obtained with the solution method. With increasing 2,4,6-TMP content up to 2.2 wt %, a decrease in polymer yield > 5 % was observed. $\overline{M}_w$ of the polymer decreased from 7.04 $\cdot 10^4$ (for P-1 obtained without 2,4,6-TMP) to 2.07 $\cdot 10^4$ (for P-6 obtained with 2.2 wt % of 2,4,6-TMP).

With increasing content of 2,4,6-TMP in solution polymerization, acting as a molecular weight regulator, an increase in dispersity was observed. At the same time *MFR* increased up to 1.51 for P-6 sample. Thermal analyses indicated that PPO obtained by solution polymerization is thermally resistant. An addition of 2,4,6-TMP caused a decrease in the glass transition temperature from 220 °C (P-1) to 205 °C (P-6).

Addition of 2,4,6-TMP to 2,6-DMP in the precipitation polymerization practically does not influence the yield of the reaction. The growth of *MFR* value was noticed. $\overline{M}_w$ of the polymers decreased by about 20 % from 4.68 $\cdot 10^4$ (for P-7 sample obtained without 2,4,6-TMP) to 3.76 $\cdot 10^4$ (for P-11 sample synthesized with 2.2 wt % of 2,4,6-TMP). Also, a decrease in T_g was detected (~ 3 °C).

Results obtained suggest that polymer properties are determined by appropriate polymerization method and required purification level of 2,6-DMP. 2,4,6-TMP is an effective molecular weight regulator in the oxidative polymerization of 2,6-DMP with the solution method if low molecular weight PPO is needed. In the precipitation polymerization an alcohol acts similarly, what determines the molecular weight of the polymer.

Polymers with the molecular weight in the range 20 000—40 000 are widely used in the industry, that is why the long and expensive 2,6-DMP purification is not needed, unless PPO with the molecular weight above 50 000 is needed (membrane application). In this case pure monomer and solution method must be employed.

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