9th International Electronic Conference on Synthetic Organic Chemistry. ECSOC-9
1-30 November 2005. http://www.usc.es/congresos/ecsoc/9/ECSOC9.HTM & http://www.mdpi.net/ecsoc/

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Microwave-assisted free radical polymerization reactions of metacrylate derivatives containing carbazole in side chain

Abstract

Free radical polymerization reactions of two carbazole unsaturated monomers with different molecular structures (vinylcarbazole and 2-(9-carbazolyl)ethyl methacrylate) were carried out under microwave irradiation and under conventional heating either. The rate of polymerization and the molecular weight depends on the structure of the monomer.

Keywords: microwave irradiation, carbazole monomers, free radical polymerization

Introduction

Considerable number of research centres has been conducting research in microwave synthesis since the mid-1980s. The number of publications concerning this subject is large and increases every year. From the beginning, scientist tried to use microwave irradiation in polymerization reactions. First investigation of this type of reactions dates back to 1983, when Teffal and Gourdene investigated the bulk polymerization of 2-hydroksyethyl methacrylate [1]. Therefore, by next twenty years, microwave irradiation has been applied in polymerization and copolymerization reactions [2-9].

Microwave irradiation has been applied in free-radical polymerization reaction of a few various unsaturated monomers. Never before any investigation concerning polymers like metacrylate derivatives containing carbazole in side chain was ran.

In our department, we are interested in synthesis of monomers and polymers under microwave irradiation, followed by copolymerization. We carried out synthesis of monomers – derivatives of carbazole and their polymerization under conventional heating. Those polymers show considerable interest for use in the organic opto-electronic devices production [10-13].

Experimental Part

Reactions were carried out in microwave reactor CEM Explorer at Department of Chemistry Vrije Universiteit in Amsterdam. This reactor allows carrying out reactions with direct temperature and pressure control during the reaction progress (Fig.1).

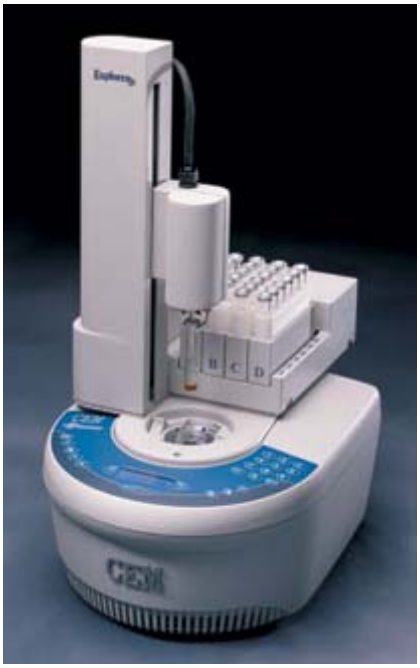

Figure 1. Microwave reactor CEM Explorer

The series of reactions were carried out for methacrylate carbazole monomers with different molecular structures (vinylcarbazole and 2-(9-carbazolyl)ethyl methacrylate).
Reactions were run simultaneously in the microwave CEM reactor and under conventional heating. We attempted to keep similar conditions in both methods.

We made investigation at different temperatures: 65^{o}C, 90^{o}C (and 120^{o}C, in case of bulk polymerization of 2-(9-carbazolyl)ethyl methacrylate). There were four solvents with different dielectric constant chosen: toluene, hexane, nitromethane, diethylene glycol as reaction environment.
We also carried out bulk polymerization for these monomers. Conditions were set up as follows:

- 1mL or 1g of monomer
- 10 minutes
- 250 W (in microwave irradiation).

There were used two systems of initiators:

– typical initiator for free-radical polymerization AIBN (2,2'–Azobisisobutyronitrile)
– system initiator - activator in ATRP method (CuBr/N,N',N',N'',N''-pentamethyldiethylenetriamine - Dimethyl 2,6-dibromoheptanedioate)
Polymerization products were precipitated and weighted for calculation of conversion

Result and Discussion

In case of solvent polymerization, we observed significant difference in yields for microwave assisted polymerization in relation to conventional heating (Table 1).
Both monomers gave higher yields under microwave irradiation than under conventional heating. It seems that the most promising were reactions with vinylcarbazole and 2-(9-carbazolyl)ethyl methacrylate in solutions. For these monomers, no product was obtained under conventional heating, despite of full conversion under microwave irradiation. (Figure 2,3)
We observed also increase of yield at higher temperature.

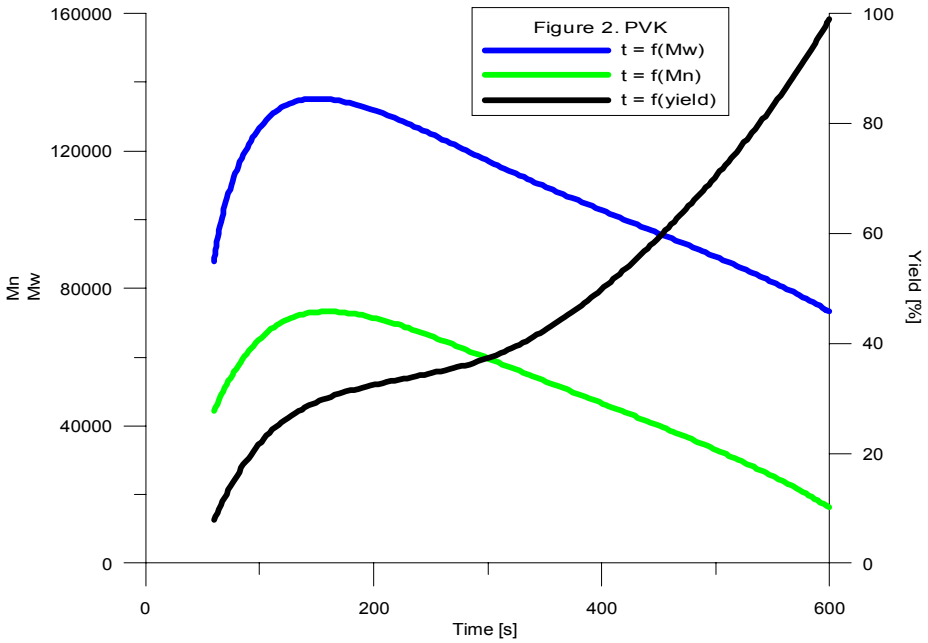

Figure 2. Dependence of molecular weight and monomer conversion on the reaction time of poly(vinylcarbazole) in toluene

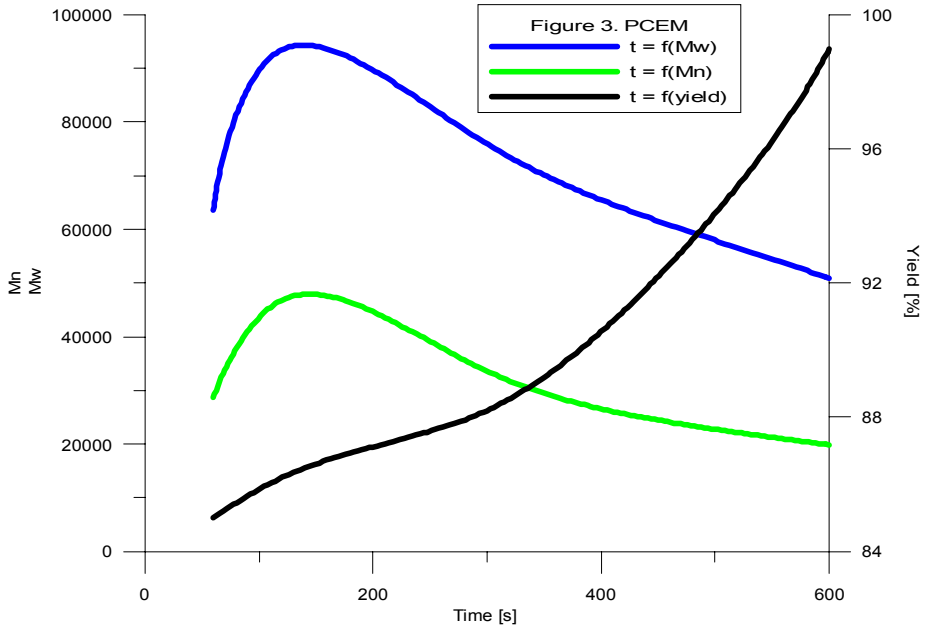

Figure 3 Dependence of molecular weight and monomer conversion on the reaction time of poly[2-(9-carbazolyl)ethyl methacrylate] in toluene

Table 1. Exemplary results for solvent polymerization

Monomer	Solvent	Yield [%]	
		MW	Δ
vinylcarbazole	toluene (65°C)	99	2
	hexane (65°C)	83	-
	diethylene glycol (65°C)	97	<1
2-(9-carbazolyl)ethyl methacrylate	toluene (65°C)	99	-
	hexane (65°C)	82	<1
	diethylene glycol (65°C)	99	-
	nitromethane (65°C)	99	-

The results of bulk polymerization didn't fulfill our expectations. The yields were similar in both methods. Reactions in ATRP gave lower yields than reactions with AIBN. In this case we expected polymers with low polydispersity index.

Conclusions

Polymerization of carbazole monomers was successfully performed using a microwave irradiation. The yields of polymerization products were higher under microwave irradiation than under conventional heating for the most reactions.

Acknowledgments

This work was supported by Polish State Committee for Scientific Research Grant No. 7T09B06521 and European Science Fundation COST Action D32 (COST-STSM-D32-00559).

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