

Syntéza styrén-akrylátových kopolymérov ako modifikátory vlastností náterových hmôt metódou RAFT

Synthesis of Styrene-Acrylate Copolymers by RAFT, Useable like Modifications of Coatings

Peter Bohacik¹, Stepan Podzimek^{1,2}, Vladimir Spacek²

¹*Institute of Chemistry and Technology of Macromolecular Substances, Faculty of Chemical Technology, University of Pardubice, Studentska 95, Pardubice 532 10*

²*Synpo a.s., S. K. Neumannna 1316, Pardubice 532 07*

Summary

This work is focused on the synthesis of random and block copolymers based on styrene and acrylic acid esters. The copolymers are prepared by Reversible addition-fragmentation Chain Transfer Polymerization (RAFT) and are characterized by size exclusion chromatography (SEC). Coating films were cast on steel panels and were evaluated by standard coatings tests. Prepared coatings show bad stability in the Q-sun tests.

Key words: RAFT, styrene-acrylate copolymers, modification of coatings

Introduction

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been well established in polymerization systems, such as bulk or solution polymerization. It is a novel technique for controlled / living polymerization. RAFT is one of the most often used synthetic polymerization methods for the preparation of well defined polymers with complex architecture. Synthesis of uniform macromolecules with precisely controlled size, novel topology, composition and functionality is a prerequisite for the specific application.^{1,2,3} Implementing RAFT polymerization can be as simple as introducing a suitable chain transfer agent – normally thiocarbonylthio compounds into a conventional free radical polymerization system. The RAFT agents used have a significant effect on the controllability of the RAFT polymerization and thus should be carefully chosen for specific polymerization system. RAFT polymerization starts with a standard initiation step as in the conventional radical polymerization, where the homolytic bond fission of a radical initiator into primary radicals occurs. Radicals react with monomer molecules to form a propagating polymeric radical P_n^* , which subsequently adds to the C=S bond of the RAFT agent and carbon-centre intermediate RAFT radical arises. Fragmentation of this intermediate gives rise to either the original reactant or polymeric RAFT compound and a new radical. The radical is able to reinitiate the polymerization and can generate its own active centre by reacting with monomer molecules, providing eventually a new polymeric radical P_m^* . Equilibrium is established between the actively growing polymeric radicals and the dormant polymeric RAFT compounds, this provides equal chance for all chains to grow and allows the production of narrowly dis-

persed polymers between thiocarbonylthio end group. The mechanism of the RAFT living polymerization is illustrated in Figure 1.⁴

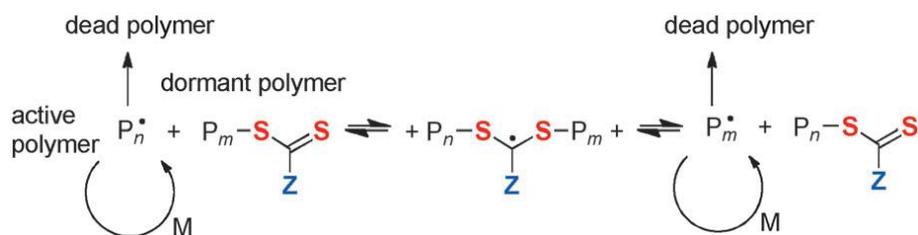


Figure 1. The principle of RAFT synthesis.

Experimental part

Polymers were synthesized of styrene (St), hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl)propyl methacrylate (TMSMAA). All the monomers were purchased from Sigma Aldrich, the Czech Republic. Before polymerization, all monomers were purified in columns with neutral activated aluminum oxide under inert gas and stored in cold and dark place. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 0.05 % wt.) was used as the initiator and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 0.095 % wt.) was utilized as the RAFT agent. All copolymers were polymerized in bulk under inert gas during 10 hours, at the temperature of 65°C. After 10 hours, the prepared polymer was cooled, purified and dried in the last step.

All polymers were characterized by SEC coupled with Optilab rEX refractive index (RI) detector, both Wyatt Technology Corporation. The RI detector operated at 658 nm. Columns Agilent PLGel Mixed C 300x7.5 mm with particle size of 5 μ m were calibrated by polystyrene standards. Samples were injected as solutions in tetrahydrofuran (THF) in the amount of 100 μ l, the concentration was approximately 3 mg/ml. All prepared solutions were filtered with 0.45 μ m filter before the injection in SEC column. Each sample was measured at 35°C.

Results

The composition and properties of prepared polymers are listed in Table 1. The averages of molar masses M_n , M_w , and M_z (g/mol), index of polydispersity \mathcal{D} , and % wt. of styrene and acrylic acid ester comonomers. Prepared polymer RAFT 1, RAFT 2, RAFT 4 and RAFT 5 were prepared by random polymerization in the bulk and RAFT 3 was prepared like block copolymer for compare properties between random and block copolymers. Coatings were prepared with thickness apt. 80 μ m on the steel panels. After 14 days were prepared coatings tested in the Q-sun for 600 hours. Coatings were containing higher part of styrene has disappeared from steel panels when test finished. Coatings were contents lower part of styrene were having yellow color with some disappeared parts. But for improvement of the properties in UV light will be better add small amount of UV stabilizator. All prepared polymers have dispersity from 1.26 to 1.42. Molar mass M_n is independent on the content of St and acrylic acid esters, but on the amount of RAFT agent. If is in the reaction mixture small amount of

RAFT agent, resultant polymer has higher molar mass M_n , M_w and M_z but have too high polydispersity. In the opposite, if is in the reaction mixture to much amount of the RAFT agent, the reaction will be stopped. RAFT agent and his amount has been chosen carefully for specific polymerization system. In the polymers who contents TMS-MAA will be trimethoxysilyl groups preserved. Were found no differences between stability of the block polymers and random polymers.

Table 1. Averages molar masses and composition of prepared polymers

Sample	Polydispersity	Molar mass of stars (g/mol)			Contents of St and ester acrylic acid		
		M_n	M_w	M_z	St	HEMA	TMS-MAA
RAFT 1	1.32	12,000	16,000	19,000	10	10	0.0
RAFT 2	1.26	20,000	25,00	31,000	15	5	0.0
RAFT 3	1.42	13,000	18,000	23,000	18	2	0.0
RAFT 4	1.34	13,000	17,000	21,000	10	0.0	10
RAFT 5	1.27	15,000	19,000	24,000	15	0.0	5

Conclusion

Before synthesized polymers by RAFT, we should found the right ratio between RAFT agent (DDMAT) and initiator (AIBN). Were prepared five polymers by RAFT polymerization. Four polymers were prepared by random polymerization and once polymer by block polymerization. Coatings films were cast on steel panel with thickness apt. 80 μm . When q-sun test stopped coatings made from RAFT 2, RAFT 3 and RAFT 4 were disappearing from steel panel. Coatings made from RAFT 1 and RAFT 5 were yellow, with some parts of disappear coatings. All coatings will be for better properties stabilized by UV stabilizers.

References

- [1] G. Moad, J. Chiefari, YK. Chong, J. Krstina, RTA. Mayadunne, A.Postma, et al. Living free radical polymerization with reversible addition fragmentation chain transfer (the life of RAFT), *Polym Int.*, 2000, 9, p993.
- [2] J. Zhu, XL. Zhu, ZP. Cheng, F. Liu, JM. Lu., Study on controlled free-radical polymerization in the presence of 2-cyanoprop-2-yl 1-dithionaphthalene (CPDN,) *Polymer.*, 2002, 43, p7037.
- [3] M. Levy, R. Milkovich, Polymerization initiated by electron transfer to monomer a new method of formation of block polymers, *J. Am. Chem., Soc.* 1956, 78, p2657.
- [4] C. Barner-Kowollik, S. Perrier, The future of reversible addition fragmentation chain transfer polymerization. *J Polym Sci Part A: Polym Chem.*, 2008, 46, 17, p5715–5723.