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«ЗЕЛЕНАЯ» КАТИОННАЯ ПОЛИМЕРИЗАЦИЯ: КАТИОННАЯ ПОЛИМЕРИЗАЦИЯ В ВОДНЫХ СРЕДАХ (ОБЗОР)

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В обзоре рассмотрены две группы катализаторов, позволяющие проводить катионную полимеризацию в присутствии воды (с использованием реагентов и растворителей без глубокой осушки) и в водных средах. Специфические кислоты Льюиса, устойчивые к гидролизу водой (BF_3OEt_2, $B(C_6F_5)_3$), катализируют контролируемую катионную полимеризацию ряда виниловых мономеров: п-метоксистирола (pMOSt), циклопентадиена (CPD) и стирола (St) в присутствии избытка воды по отношению к кислоте Льюиса (LA). В указанных условиях были синтезированы полимеры с контролируемой молекулярной массой (до $M_n \sim 10000$ Да) и относительно узким молекулярно-массовым распределением M_w/M_n: <1,3; <1,2–1,6; <1,5–1,8 для pMOSt; CPD; St соответственно.

Каталитические системы на основе $B(C_6F_5)_3$ позволили впервые провести катионную полимеризацию целого ряда виниловых мономеров в водных средах: pMOSt, п-гидроксистирола (pHOSt), St, CPD и изопрена (IP). Полимеризация pMOSt и pHOSt протекает в режиме «живых» цепей, позволяя синтезировать полимеры с M_n<4500 Да, концевыми гидроксильными группами и низкой полидисперсностью (M_w/M_n < 1,5). Полимеризация St, CPD и IP осуществляется через контролируемое инициирование и необратимый обрыв цепи через воду с образованием функционализированных олигомеров (M_n < 2000 Да), молекулярная масса которых определяется их поверхностной активностью и полярностью границы раздела фаз.

Открытие катализаторов на основе комплексов солей редкоземельных металлов (YbX_3, где X — Cl, NO_3, OTf) и хлоридов In (III), Sc(III), Y(III) с сильно разветвленным додецилбензолсульфонатом натрия (Lewis acid surfactant combined catalyst (LASC)) предоставило новые возможности для катионной полимеризации, позволив впервые синтезировать гомополимеры с высокой молекулярной массой (M_n от 36000 Да до 200000 Да), а также статистические и мультиблоксополимеры St с IP или β-мирценом (M_n = 50000–150000 Да) методом эмульсионной катионной полимеризации в мягких условиях.

Ключевые слова: катионная полимеризация; кислоты Льюиса; вода; катализаторы; стирол и его производные; 1,3-диены.

«GREEN» CATIONIC POLYMERIZATION: CATIONIC POLYMERIZATION IN AQUEOUS MEDIA (REVIEW)

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In this review, two types of catalysts allowing to conduct the cationic polymerization in the presence of water (using reagents and solvents without any purification) and in aqueous media have been reported. Specific Lewis acids stable in water such as BF_3OEt_2 and $B(C_6F_5)_3$ induced controlled cationic polymerization of

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a number of vinyl monomers (p-methoxystyrene (pMOSt), cyclopentadiene (CPD) and styrene (St)) in the presence of excess of water towards Lewis acid. The polymers with controlled molecular weight (up to M_n~10000 Da) and relatively low polydispersity(M_w/M_n: <1.3 (pMOSt), 1.2–1.6 (CPD) and 1.5–1.8 (St).

Using of $B(C_6F_5)_3$-based catalytic systems allowed to conduct for the first time the cationic polymerization of great variety of vinyl monomers in aqueous media such as p-methoxystyrene (pMOSt), p-hydroxystyrene (pHOSt), cyclopentadiene (CPD), styrene (St) and isoprene (IP). Polymerization of pMOSt and pHOSt proceeds in a living fashion resulting in hydroxyl-terminated polymers with M_n < 4500 Da and low polydispersity (M_w/M_n < 1.5). Polymerization of St, CPD and IP occurs via controlled initiation followed by irreversible chain transfer to water with the formation of functionalized oligomers (M_n < 2000 Da), molecular weight of which governs by surface activity and polarity of the interface.

Discovery of catalysts based on complexes of rare earth metal salts (YbX_3, X = Cl, NO_3, OTf) and chlorides of In (III), Sc(III), Y(III) with hyperbranched sodium dodecylbenzenesufonate (Lewis acid surfactant combined catalyst (LASC)) opens new possibilities for cationic polymerization allowing to prepare for the first time polymers with high molecular weight (M_n from 30000 Da to 200000 Da) as well as random and multiblock copolymers of St with IP and β-myrcene via emulsion cationic polymerization under mild conditions.

Keywords: cationic polymerization; Lewis acids; water; catalysts; styrene and its derivatives; 1,3-dienes.

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