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Synthesis of graft- and star like polymers using functionalized methacrylates

The aim of the work was to find an easy reaction way to graft and star like polymers, consisting of styrene and butyl acrylate. The idea to reach this goal was to use coupling reactions between functionalized polymer chains. The active groups, which are necessary for the coupling reaction should be introduced into the polymer using functionalized methacrylates.

For the synthesis of graft polymers via the "grafting onto"-method, functionalized backbones were synthesized by radical copolymerisation of glycidyl methacrylate (GMA) and 2-hydroxyethyl methacrylate (HEMA) with styrene (S) or butyl acrylate (BuA). In TEMPO mediated free radical copolymerizations of styrene with glycidyl methacrylate, backbones (M_n < 40.000 g/ mol) with low polydispersities (PD < 1.35) and up to 30 mol% GMA were produced. Taking dicumyl peroxide as additional initiator it was possible to increase the amount of GMA up to 50 mol% in the backbones receiving these narrow polydispersities.

The disproportionation reaction, a side reaction of the TEMPO mediated free radical polymerization of methacrylates, which was well investigated for butyl acrylate by Burguiere et al.[1], could be used successfully to convert TEMPO terminated polymers into end functionalized polymers. The reaction leads to the formation of ω-unsaturated polymers as a result of hydrogen abstraction from the propagating polymer radicals by the nitroxide radicals. In good agreement with the results of Burguiere et al.[1], it was found that the number of functionalized monomer units attached to the backbone is directly related to the TEMPO concentration during the disproportionation reaction. Using this way, polystyrenes with molecular weights M_n = 3200-20.000 g/ mol were functionalized with different numbers of epoxide and alcohol groups. The characterization of the products by ^{1}H-NMR, FTIR, elemental analysis and GPC has shown, that by variation of the free TEMPO concentration in the range of 0.5 – 5 mmol/ L 3 - 19 monomer units can be attached per polymer chain end. This method leads also to end functionalized PS-*b*-P(S-*co*-BuA) copolymers with an amount of 50 -70 mol% butyl acrylate in the copolymer block. The PS-*b*-P(S-*co*-BuA)

copolymers were synthesized in a TEMPO mediated free radical suspension copolymerization of butyl acrylate with styrene using a TEMPO terminated polystyrene macro initiator. After adopting the results of previously investigated functionalization reactions to these block copolymers it was possible to introduce end functionalities into the polymer. It was found that with an increasing amount of butyl acrylate in the copolymer block (20-80 mol%) the average number of attached methacrylate units decreases from 39 to 4.

For the determination of the optimal reaction parameters for the coupling reactions between functionalized polymer chains, epoxy functionalized polystyrenes were converted with hydroxy functionalized polystyrenes (M_n = 8000 -12.000 g/ mol) under basic and acidic conditions. By activation with sodium hydride or boron trifluoride coupling products were synthesized under mild conditions. With sodium hydride an almost complete conversion of the starting materials could be achieved. Due to several functional groups per chain end star like polymers were formed. Molecular weight distribution curves of different coupling processes were achieved by PREDICI simulations of the product. It could be shown that also reactions between coupling products themselves took place.

The transfer of the reaction conditions to coupling reactions between end functionalized PS-*b*-P(S-*co*-BuA) copolymers with molecular weights of approx. 70.000 g/ mol showed that no coupling product was produced by catalysis with sodium hydride. An increase of the reaction temperature leads to cross linked polymers by ester condensation reactions of butyl acrylate units. Using boron trifluoride as activating agent coupling products were formed.

Because of disproportionation reactions between butyl acrylate radicals and TEMPO during the suspension polymerization the conversion of polymer chains in the following coupling reactions depends on the copolymer composition. The larger the amount of butyl acrylate the smaller the conversion. Due to the prehistory of the end functionalized PS-*b*-P(S-*co*-BuA) block copolymers it can be assumed that a complete conversion can not be realized. Due to incomplete coupling reactions in all experiments bimodal molecular weight distributions were observed. Besides, the peaks

of not converted polymers, a second peak with a clear high-molecular weight becomes visible. The mass of the polymers does not change during the coupling reactions. Therefore, the molecular weight distribution of the pure starting material can be fitted into those of the product and the molecular weight distribution of the coupling product can be received. After the separation of the reaction product from the reaction mixture using preparative gel permeation chromatography or by fractionated precipitation the pure coupling product was obtained. Characterization of the resulting products showed that star like polymer structures of more than 10 arms per molecule and with polydispersities of approx. 1.3 were synthesized. Due to the strong contraction of the coils of star like polymers compared with linear polymers of same molecular weight, it is not possible to determine the actual molecular weights by gel permeation chromatography, which was calibrated with linear polystyrene standards. Despite of the high molecular weights of the coupling products no micro phase separation of the styrene and the butyl acrylate phases is observable.

The reaction of P(S-*co*-GMA) backbones with hydroxy functionalized polystyrenes to P(S-*co*-GMA)-*g*-PS led only to small conversions of graft polymers. By the use of P(S-*co*-HEMA) as well as P(BuA-*co*-HEMA) backbones in coupling reactions with epoxy functionalized polystyrenes in the presence of boron trifluoride, graft polymers with up to 7 and 37 side chains per backbone were produced.

References

[1] Burguiere, Dourges, Charleux, Vairon *Macromolecules* 1999, **32**, 3883