

High-T-g Functional Aromatic Polymers

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Abstract

A novel series of linear, high-molecular-weight polymers and copolymers were synthesized by one-pot, metal-free superacid-catalyzed polymerization of aliphatic 1,2-diketones (2,3-butanedione (1a), 2,3-hexadione (1b), 3,4-hexadione (1c), 2,3-butanedione monoxime (1d), pyruvic acid (1e), 1,4-dibromo-2,3-butanedione (1f), 2-bromopyruvic acid (1g), and methyl-3,3,3-trifluoropyruvate (1h) with linear, nonactivated, multiring aromatic hydrocarbons terphenyl (A), biphenyl (B), fluorene (C), and N-ethyl carbazole (D). Depending on the reaction system, the polymerizations were carried out as stoichiometric or non stoichiometric, with direct or inverse monomer addition. Copolymers were obtained by polymerization of 1,2-diketones with a mixture of aromatic hydrocarbons. In the course of the polymerization only one carbonyl group of a 1,2-diketone reacts to form C–C bonds with aromatic fragments while the other functional groups (including the second carbonyl group) are incorporated unchanged into polymer chain. The polymerizations performed at room temperature in the Brønsted superacid CF₃SO₃H (TFSA) and in a mixture of TFSA with methylene chloride or trifluoroacetic acid (TFA) tolerant of carbonyl, acetyl, N-oxime, carboxy, methoxy, and bromomethyl groups. The polymers obtained were soluble in most common organic solvents, and flexible transparent, colorless films could be cast from the solutions. ¹H and ¹³C NMR analyses of the polymers synthesized revealed high regio-selectivity of the polymerizations and yielded linear structures with para-substitution in the phenylene fragments of the main chains. An electron affinity (EA) of the carbonyl component and the heterolytic C–O bond dissociation energy (DE) in carbinol 3 (correlating with the activation energy of carbocation 4 formation) have been used to rationalize the reactivity of carbonyl components. The calculations show the following reactivity order of the diketones. 1f > 1g ≈ 1e > 1a > 1d > 1h > 1b > 1c which is totally in agreement with the experimental data. The new functional polymers obtained demonstrate good processability, high T_g and thermal stability. Unexpected white light emission was observed for polymer 2gA.