Macromolecules **1991**, *24*, 3973–3974

Spontaneous Copolymerization of [1.1.1]Propellane with Electron-Poor Monomers

Introduction. The tricyclo[1.1.1.0]pentane, simply known as [1.1.1]propellane, has recently become available in research quantities. This compound, despite its extremely strained structure, is reasonably stable even at room temperature.[1] However, the bond between the two bridged carbon atoms easily undergoes free-radical addition ractions.[2] A large local charge concentration at the bridgeheads of [1.1.1]propellane is responsible for ring-cleavage reactions breaking the bridgehead C–C σ bond.[3–6] Free-radical addition reactions are possible with electron-deficient alkenes. Copolymerization of the trimethylene derivative of a bridged [1.1.1]propellane with acrylonitrile and the [1.1.1]propellane with maleic anhydride was reported as a free-radical addition leading to an alternating copolymer.[6,7] In our laboratory, we have been exploring the usefulness of [1.1.1]propellane for the synthesis of new polymeric materials, since the [1.1.1]propellane is an interesting and versatile building block.

In the present investigation we report the copolymerization of the [1.1.1]propellane with electron-deficient monomers like methyl methacrylate, methyl acrylate, vinyl acetate, etc. Preliminary findings are presented about the effect of various synthetic parameters (ratio of monomers, temperatures, etc.) on the properties of the copolymers.

Experimental Section. Materials. Methyl methacrylate, methyl acrylate, vinyl acetate (Aldrich Chemical Co.), and *tert*-butyl methacrylate (Rome Tech Monomers) were distilled and used. [1.1.1]Propellane was prepared from 1,1-bis(chloromethyl)-2,2-dibromocyclopropane by following the procedure described by Michl et al.[8] and Schluter et al.[9] All solvents used in this work were AnalaR reagents obtained from Aldrich. They were distilled before use.

Instruments. ^{1}H NMR spectra were obtained on a General Electric QE 300 spectrometer, using $CDCl_3$ as solvent. Molecular weights of the copolymers were determined by using a Spectra-Physics GPC with an IsoChrom LC pump, a SP-4270 integrator, and a SP-8430 refractive index detector, equipped with three phenogel columns in series, 250 × 8 mm (i.d.), 10-μm particle size. THF was used as the mobile phase at a flow rate of 1 mL/min. Polystyrene standards were obtained from Pressure Chemicals. Viscosity measurements were carried out by using an Ubbelohde viscometer with a photoelectric registration of flow times. Thermogravimetric analysis and differential scanning calorimetric measurements were made by using a Perkin-Elmer Series 7 thermal analysis system at a heating rate of 10 °C/min in a nitrogen atmosphere.

Preparation of Copolymers. The calculated amounts of [1.1.1]propellane in pentane or diethyl ether and of an electron-deficient monomer were vacuum transferred into a cooled ampule equipped with a Rotaflow tap. The ampule was removed from the vacuum line and allowed to warm up to room temperature. The polymerization was performed at a specified temperature in a controlled-temperature bath. After an induction period, the colorless clear liquid started precipitating. After completion of precipitation, the supernatant liquid was distilled off under vacuum, the copolymer was removed by dissolving in THF, precipitated in methanol, filtered, and dried under vacuum. The amounts of the monomers and the reaction conditions are reported in Table I. When a chain-transfer agent or radical inhibitor was added, it was added to the ampule at the beginning before the monomers were transferred into it. The composition of the copolymers was estimated from the ^{1}H NMR spectra and from elemental analysis. The properties of the copolymers were studied by gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, etc.

Table I
Preparation of Copolymers[a]

code	comonomer	solvent	temp, °C	remarks
A1	MMA (5)	pentane	20	
A2	MMA (5)	pentane	40	
A3	MMA (5)	pentane	60	
A4	MMA (123)	pentane	20	
A5, A6	MMA (5)	pentane	20	in dark
A7	MMA (1)	pentane	20	
A8	MMA (5)	pentane	20	with $CHCl_3$ (0.08)
A9, A10	MMA (5)	diethyl ether	20	
B1	MA (5)	pentane	20	
B2	MA (1)	pentane	20	
B3	MA (5)	diethyl ether	20	
C1	tBMA (5)	pentane	20	
D1	VA (5)	pentane	20	

[a] Numbers in parentheses are molar ratios in the initial mixture refering to propellane.

Table II
Molecular Weight, Composition, and Intrinsic Viscosity of Copolymers

		propellane mol fractions, %		intrinsic viscosity, mL/g	
copolymers	$M_w/10^5$ [a]	from NMR	from CH anal.	25 °C	20 °C
A1	6.9	49	50	427	527
A2	5.4	45			397
A3	3.4	48		213	254
A4	2.7	34		80	
A5	10.3	44			
A6	6.8	35			336
A7	1.4	49		166	
A8	3.6	35	34	88	
A9	0.4	47			
A10	1.5	39	40		130
B1	6.7	46	43	328	
B2		43	48		
B3	0.5	53	38		
C1	3.5	50	50		
D1		65	70		

[a] Values are calculated from GPC by using a polystyrene calibration curve.

Results and Discussion. The synthesis of the copolymers was carried out at different temperatures. There was no copolymerization at low temperature (–76 °C) even after 10 days. In the beginning of the polymerization at higher temperatures, the mixture of monomers formed a homogeneous colorless clear solution. After the induction period (about 30 h at 20 °C) it became turbid and started to precipitate. The induction period decreased with increasing temperature. Copolymerization proceeded in the dark as well as in the presence of anionic polymerization impurities (e.g., methanol) at 20 °C but not in the presence of a radical inhibitor (hydroquinone). This indicates the polymerization proceeded by a radical mechanism. According to the GPC results, the molecular weight of the copolymers was in the range of 10^5–10^6 (Table II). The presence of small amounts of chain-transfer agent (chloroform) during polymerization did not lower the molecular weight appreciably. All the copolymers prepared in this study are soluble in organic solvents, e.g., tetrahydrofuran, chloroform, etc. The compositions of copolymers were established by ^{1}H NMR and elemental analysis. The

0024-9297/91/2224-3973$02.50/0

Table III
Glass Transition (T_g) and Decomposition Temperatures (°C) of Copolymers

copolymers	T_g[a]	start of decompsn	10% loss	50% loss	90% loss
A1	169	290	343	383	408
B1	139	230	333	378	396

[a] T_g of homopolymers: PMMA, 105; PMA, 10.

results from NMR spectra and elemental analysis agree well. The data indicate that the copolymers have a strong alternating tendency. Nevertheless, when a very large excess of the monomer was used, the content of propellane in the copolymer was slightly less than 50 mol %. The intrinsic viscosity of copolymers increases with increasing propellane content in the copolymer (at a constant molecular weight). Thermal behavior was studied by TGA and DSC (Table III). Methyl methacrylate–propellane copolymer started decomposing at 290 °C, whereas methyl acrylate–propellane copolymer started decomposing at 230 °C. These temperatures are rather high; this is in agreement with the decomposition temperature of bicyclopentane at 305 °C.[10] The DSC traces showed that the glass transition temperatures of the copolymers are much higher than the T_g values of the corresponding acrylic homopolymers probably due to the presence of rigid propellane units.

Preliminary experiments indicate that [1.1.1]propellane copolymerizes also with other monomers. These results will be published later.

Acknowledgment. This investigation was supported by Grant No. DMR-8807701 from NSF.

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Received February 26, 1991