CHEMISTRY LETTERS, pp. 1145−1148, 1991.

Synthesis of Thermally Stable Vinyl Polymers from Adamantyl-Containing Acrylic Derivatives

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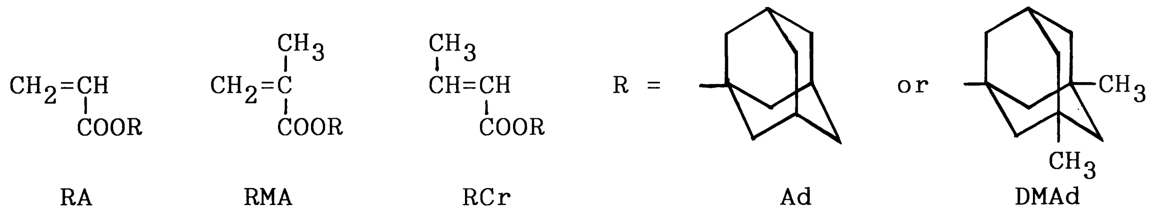
1-Adamantyl and 3,5-dimethyl-1-adamantyl acrylates, methacrylates, and crotonates were polymerized through radical or anionic mechanism. Thermally stable and less-flexible vinyl polymers were obtained, depending on the structure of the repeating monomer units.

Adamantane is a thermodynamically stable and highly symmetrical tricyclic hydrocarbon, which consists of fused chair-form cyclohexane rings.1) Some polymers bearing an adamantyl moiety in their main or side chains have been prepared,2,3) because adamantane has unusual physical and chemical properties, e.g., thermal and oxidation stabilities, high density, hydrophobicity, and low surface energy.

We have reported since 1981 on synthesis of poly(substituted methylene)s through radical polymerization of fumaric and maleic derivatives.4) It has been found that the polymerization reactivity of dialkyl fumarates (DRF) depends on the bulkiness of the ester alkyl groups, i.e., di-*t*-butyl ester shows the highest polymerization rate and molecular weight of the resulting polymer. It was revealed that increase of the reactivity by introduction of bulky groups was due to decrease in the bimolecular termination rate between polymer radicals by rotating sector method and ESR spectroscopy. The rigidity and tacticity of the polymer were also intensively dependent on the kind of the ester alkyl groups.5,6) A similar semiflexible polymer has been also prepared by anionic polymerization of *t*-butyl crotonate.7,8)

In this study, we have examined on radical and anionic polymerizations of some adamantyl-containing acrylic derivatives, i.e., acrylates (RA), methacrylates (RMA), and crotonates (RCr) as shown in Scheme 1. The polymerization reactivity and thermal property are clarified and discussed in the relation to the structure of the monomers and polymers.



Scheme 1.

All monomers were obtained in a high yield (80-95%) by the reaction of a corresponding acid or anhydride with 1-hydroxyadamantane or 1,3-dimethyl-5-hydroxyadamantane by the most conventional method, i.e., reflux in cyclohexane for several hours with removing water in the presence of an acidic catalyst.

In Table 1, the results of radical and anionic polymerizations of these acrylic monomers are summarized. In radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as an initiator, the polymerization rate of RA and RMA increased by the introduction of adamantyl groups compared with those for other alkyl esters, e.g., methyl, *t*-butyl, and cyclohexyl, and the increase in number-average molecular weight of the polymer was also observed in proportion to the rate.[9)] It is interpreted by the decrease in termination rate between polymer radicals. In fact, it has been verified by the direct observation of ESR spectrum of propagating polymer radical of RMA under usual polymerization conditions.[9)]

Anionic polymerization of RMA was also performed with *s*-butyllithium (sBuLi) in toluene and tetrahydrofuran (THF). The methanol-insoluble polymer was produced quantitatively owing to the prevented side reaction such as formation of vinyl ketone by attack of the alkyllithium to the carbonyl group on account of the steric hindrance of the adamantyl group. RCr, which is β-*trans*-methyl-substituted acrylate as an isomer of RMA, is well-known not to homopolymerize radically, but anionic polymerization of *t*-alkyl esters is initiated with alkyllithiums to yield high molecular weight polymers.[7,8)] The adamantyl esters were also polymerized similarly to give high molecular weight polymer in high yields.[10)]

All of the adamantyl-containing polymers produced are colorless powder and soluble in benzene, toluene, chloroform, and THF. It has been revealed by differential scanning calorimetry that their glass transition temperatures (T_g) are extremely high. The T_g increased in the following order; poly(RA) < poly(RMA) < poly(RCr), which reflects the rigidity of the chain and is consistent with the steric hindrance of the methyl groups on the main chain. The chain rigidity of poly(RMA) has been evaluated from intrinsic viscosity in several solvents, i.e., the characteristic ratio for

Table 1. Radical and Anionic Polymerizations of Acrylic Derivatives Bearing Adamantyl Esters and Thermal Properties of the Resulting Polymers

Monomer	R	Initiator	Solvent	Temp	Time	Conv	M_n a)	T_g	T_{init}	T_{max}
		mmol L^{-1}		°C	h	%	x 10^{-4}	°C	°C	°C
RA b)	Ad	AIBN(1)	Benzene	60	1.3	53.6	19.1	153	292	437
	DMAd	AIBN(1)	Benzene	60	1	53.2	23.9	105	285	426
RMA b)	Ad	AIBN(1)	Benzene	60	1	12.8	39.1	>dec	254	304
	Ad	sBuLi(28)	Toluene	-78	5	$\approx$ 100	0.6	183	284	405
	Ad	sBuLi(15)	THF	-78	1	$\approx$ 100	3.3	>dec	261	298
	DMAd	AIBN(1)	Benzene	60	1	13.8	41.0	194	239	347
RCr c)	Ad	sBuLi(16)	THF	-78	1	99.1	0.8	>dec	305	428
	DMAd	sBuLi(16)	THF	-78	1	74.7	1.1	230	308	418

a) Number-average molecular weight by gel permeation chromatography in THF. b) [Monomer] = 1 molL^{-1}. c) [Monomer] = 0.2 molL^{-1}.

the adamantyl esters of poly(RMA), which represents local chain conformation in an unperturbed dimension, is much larger than the values reported for other polymethacrylates such as methyl and cyclohexyl esters.11)

The 3,5-dimethyl-substituted derivatives always have lower T_g values than the respective unsubstituted polymers, i.e., the adamantyl esters of poly(RMA) and poly(RCr) do not show T_g below their decomposition temperatures ($\approx$250 °C and $\approx$300 °C, respectively), but T_g decreases to 194 and 230 °C for poly(RMA) and poly(RCr), respectively, by the 3,5-dimethyl-substitution. Similar effect was also observed for poly(RA), i.e., lowering from 153 °C to 105 °C.

In the case of poly(RMA), the T_g was intensively influenced by tacticity. It has been clarified by NMR spectroscopy that the adamantyl ester of poly(RMA) prepared by anionic polymerization in toluene at -78 °C is isotactic, i.e., triad tacticity was mm:mr:rr = 88:10:2, whereas the polymer produced in THF had that of 13:38:49. It has been also confirmed that the poly(RMA) prepared by radical polymerization is predominantly syndiotactic, mm:mr:rr = 3:30:67. The results in Table 1 indicate that the isotactic poly(RMA) has lower T_g (183 °C) than syndiotactic one. It is reasonable because similar tendency is also observed for poly(methyl methacrylate) and others.12)

The decomposition of these adamantyl-containing acrylic polymers was investigated by thermogravimetric analysis in a nitrogen stream with a heating rate of 10 °Cmin^{-1}. The initial and maximum decomposition temperatures (T_{init} and T_{max}) are listed in Table 1. They have high T_{init} (250-300 °C) and T_{max} (300-440 °C) because of the thermodynamic stability of the adamantyl linkage, although polymers bearing *t*-alkyl esters generally tend to eliminate olefins at a relatively low temperature.[13)]

The detailed discussions on polymerization of RMA and RCr and characterization of the polymers will appear elsewhere.[9-11)]

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(Received April 15, 1991)