

SOME NEW LINEAR AND BRANCHED POLYMERS

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Abstract - With radical initiators, 2-isopropenylnaphthalene can only be copolymerized, for example with maleic anhydride, maleimide, acrylonitrile, n-butylmethacrylate, or butadiene. With butyllithium, linear homopolymers having molecular weights up to 300,000 and very narrow distribution are obtained. Their glass transition temperature is about 220°C. Since the polymerization proceeds via "living polymers", diblock and triblock copolymers are available. Triblock copolymers with butadiene are thermoplastic elastomers.

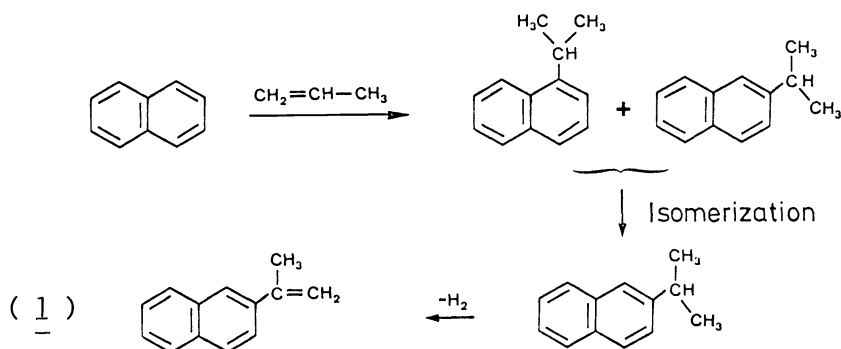
Synthesis and cationic polymerization of two unsaturated cyclic acetals are described. 4H,7H-Dioxepine forms linear polymers with cis 1,4-butadiene units in the main chain. These polymers as well as copolymers of this monomer with dioxolane or trioxane can undergo several addition reactions at the double bonds. Thus, a chemical modification or a cross-linking of acetal polymers is possible.

The metalation of some polyamides and the alkylation at the N-atom are described. With these methods comb-like polymers with well-defined branching points and definite length of the branches are obtained. Polyamides with long side chains exhibit side chain crystallinity. N-alkylated linear polyethyleneimine is another example of comb-like polymers. These polymers form organic soluble chelate complexes with transition metal salts.

POLYMERIZATION OF 2-ISOPROPENYLNAPHTHALENE

The ability of 2-isopropenylnaphthalene (1) to polymerize has been known for over 20 years. Due to the inconvenient synthesis of this monomer on a laboratory scale, its polymerization behavior has scarcely been evaluated; in contrast to well-known analogous compounds such as α -methylstyrene and 2-vinylnaphthalene (Ref. 1-5).

Recently, a novel commercial synthesis of 1 has been developed (Ref. 6) with naphthalene and propene as starting products. This monomer (99% purity, m.p.: 54°C), has been utilized for our experiments.



In accordance with earlier investigations, it was impossible to homopolymerize 1 with radical initiators. Copolymerizations, however, are feasible. A mixture of maleic anhydride and 1 in an organic solvent at room temperature (Ref. 4) forms a yellow-colored charge-transfer complex. The equilibrium constant of complex formation is 0.23 kg/mol ($\pm 4\%$), as measured by UV and $^1\text{H-NMR}$ spectroscopy (solvent: CH_2Cl_2). In toluene at 60°C with AIBN as initiator, 1 and maleic anhydride react to form a mixture of a crystalline and an amorphous substance. The crystalline material is a 1:1 Diels-Alder (DA) adduct, the amorphous substance is a copolymer. According to elemental analysis, this copolymer has an alternating structure, but the yield of copolymer is very small. An initiator system comprising triethylborane and cumenehydroperoxide at $0 - 20^\circ\text{C}$ favors the formation of copolymer with respect to DA adduct (Ref. 8). With AIBN at 50°C , maleimide and 1 form an alternating copolymer having a molecular weight of ca. 20,000. This copolymer (m.p. ca. 300°C (Ref. 8)) is soluble in THF, DMSO, DMF, dioxane, and acetone.

The copolymerization of 1 with acrylonitrile has first been described by Doak et al. (Ref. 1). Our experiments (Ref. 9,10) confirmed the results of these investigators. With increasing amounts of 1 in the monomer mixture, the polymerization rate and the molecular weights of the copolymers decreased.

The radical copolymerization of 1 with n-butylmethacrylate was very extensively investigated in the author's laboratory (Ref. 10). After 10-20 hours in toluene at 60°C , maximum yields of ca. 10% were obtained (initiator: AIBN). In contrast, the emulsion copolymerization with $\text{K}_2\text{S}_2\text{O}_8$ proceeds much faster yielding high molecular weights. The composition of these copolymers can be evaluated by pyrolysis gas chromatography (Ref. 11). Poly-2-isopropenylnaphthalene (poly-1) above 310°C depolymerizes quantitatively forming the monomer (Ref. 12). When a copolymer of 1 and n-butylmethacrylate is pyrolyzed at 700°C , the corresponding GLC chart exhibits two well-separated peaks. By means of a calibration curve, the copolymer composition can then be calculated from the area ratio of the peaks. Copolymerization parameters determined according Kelen-Tüdös are compiled in Table 1. The copolymerization of 1 with butadiene is also quite advantageously carried out in emulsion at 60°C with $\text{K}_2\text{S}_2\text{O}_8$ as initiator. Conversions up to 60% are obtained. Depending on the reaction conditions, the copolymers contain 6-65 mol % 1 (see Table 1 for $r_1 - r_2$ values).

TABLE 1. Radical Copolymerization of 2-Isopropenylnaphthalene (M_1)

M_2	solvent	temp. °C	initiator	r_1	r_2	Ref.
maleic anhydride	toluene	60	AIBN	~ 0	~ 0	7,8
"	"	0-20	BEt ₃ /CHP ^{a)}	~ 0	~ 0	8
maleimide	THF	-15 to 15	AIBN/h ν	~ 0	~ 0	7,8
"	THF	50	AIBN	~ 0	~ 0	8
acrylonitrile	toluene	80	AIBN	0,23	0,05	1,9
"	"	80	AIBN	0,26	0,04	10
n-butylmethacrylate	"	80	AIBN	0,07	0,54	10
"	emulsion	60	K ₂ S ₂ O ₈	0,31	0,42	10
butadiene	"	60	K ₂ S ₂ O ₈	0,40	0,74	10

a) CHP = cumenehydroperoxide

It is known that α -methylstyrene and 2-vinylnaphthalene can be cationically polymerized. Therefore, we attempted to polymerize 1 under similar conditions. With BF₃·OEt₂, SnCl₄, or CF₃-SO₃H in methylene chloride at -20⁰ to +20⁰C the monomer was consumed very rapidly. However, GPC reveals that only oligomers (degree of polymerization 2-5) are formed (Ref. 12). Similar results were obtained by Marechal et al. (Ref.5).

Attempts to cationically copolymerize a 1:1 mixture of 1 and styrene also resulted in the formation of a mixture of oligomers of 1. According to Hopff and Lüssi (Ref. 2), 1 was polymerized with anionic initiators. The authors reported a ceiling temperature of $T_c = 23,9^0C$. We could confirm this number (Ref. 13), but also found that T_c is a function of the molecular weight. Upon addition of BuLi to a carefully dried solution of 1 in THF below 0⁰C, a deep-green color is formed (Ref.14). After addition of methanol, colorless polymers are obtained in quantitative yield. Molecular weights of 13,000 - 870,000 were determined by light scattering measurements. Furthermore, a GPC calibration curve (polystyrene standards) was used for evaluating M_w and M_n of poly-1. The ratio M_w/M_n lies in the range 1.06 - 1.20. This means that poly-1 is formed via a "living polymerization". Viscosity measurements yielded the constants of the η -M relation $[\eta] = K \cdot M^a$ at 25⁰C:

in THF: $K = 1.434 \cdot 10^{-2}$ ml/g; $a = 0.663$

in toluene: $K = 1.538 \cdot 10^{-2}$ ml/g; $a = 0.646$.

Comparing the glass transition temperature of polystyrene ($T_g: 90^0C$), poly- α -methylstyrene ($T_g: 185^0C$) and poly- β -vinylnaphthalene ($T_g: 151^0C$), a high T_g of poly-1 ought to be expected. As a matter of fact, depending upon the molecular weight, T_g values between 200 and 220⁰C are obtained (Table 2.).

TABLE 2. Molecular weights, viscosity numbers and glass transition temperatures of poly-2-isopropenylnaphthalene obtained by polymerization with n-butyl-Li in THF

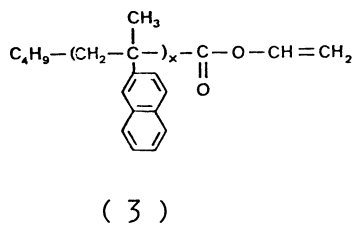
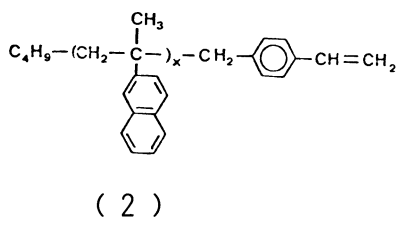
sample	$[\eta]$ (cm^3/g)	M_w (GPC)	M_n (GPC)	M_w/M_n	T_g ($^{\circ}\text{C}$)
101	59.09	309,500	278,200	1.11	220
102	43.96	204,600	182,900	1.12	219
157	40.23	170,900	157,000	1.09	-
159	37.20	142,200	134,900	1.06	-
114	17.91	49,600	46,400	1.07	216
106	15.30	40,700	37,900	1.07	215
115	13.06	30,700	28,400	1.08	213
104	7.91	13,900	11,700	1.19	204

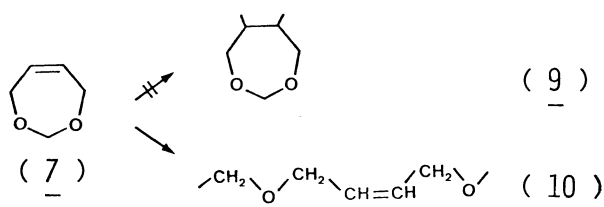
Extrapolation of $1/M_w$ toward zero yields $T_{g\infty} = 221^{\circ}\text{C}$. As mentioned before, at temperatures above 300°C thermal degradation of poly-1 under reformation of the monomer takes place. One further very exciting physical property of the polymer is its luminescence (Ref.15). The fact that the anionic polymerization of 1 proceeds via living polymers, opens the possibility of synthesizing block copolymers. First, we investigated diblock and triblock copolymers with butadiene as comonomer (Ref.16). The butadiene blocks can amount to 10 - 95% (with 85% of 1,2-structures).

Electron microscopy reveals the phase separation into lamellar or insular structures. The triblock copolymers are thermoplastic elastomers in analogy to the well-known styrene-butadiene-styrene triblock copolymers.

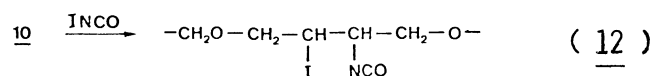
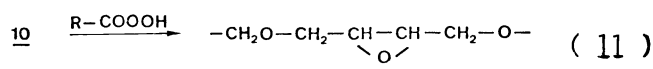
Du to the high glass transition temperature of the poly-1 blocks, the rubber elastic region covers the range of 0-190 $^{\circ}\text{C}$.

Further investigations as to block copolymers comprising polysiloxane and polyethyleneoxide blocks are presently underway (Ref.13). In addition, the living polymerization of 1 renders the possibility of synthesizing macromers. By chain termination with appropriate reagents, we thus have obtained the macromers 2 and 3 (Ref.17).

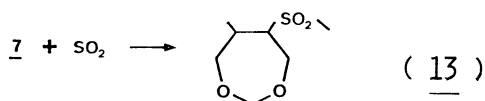




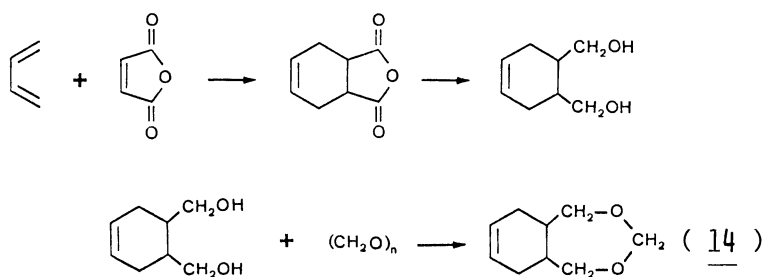
This means that exclusively a ring-opening polymerization has taken place (10). A vinyl polymerization (9) can definitely be ruled out. Monomer 7 can be copolymerized with arbitrary amounts of trioxane or dioxolane yielding polyacetals with the desired number of reactive double bonds in the main chain (Ref.23). A great number of reactions can be carried out at the double bonds of poly-7 and the copolymers (Ref. 22,23). Reaction with percarboxylic acids yields polymers with epoxide moieties (11). The addition of iodo isocyanate gives polymers with pending isocyanate groups. Both types of modified polyacetals can afterwards be cross-linked by diamines (Ref.23).



A radical homopolymerization of the double bond of 7 is impossible. The radical copolymerization of 7 with maleic anhydride, however, was the subject of a recent publication (Ref.24). Moreover, we investigated the radical copolymerization of 7 with acrylonitrile or SO₂ using AIBN as catalyst. The SO₂-containing copolymers are polysulfones (13)(Ref.23).

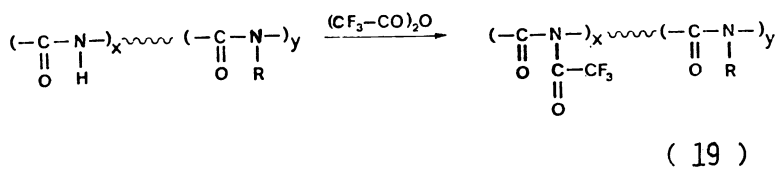


A bicyclic unsaturated acetal (14) was synthesized starting from butadiene and maleic anhydride (3,5-dioxabicyclo-5.4.0 undec-9-ene)(Ref.25). 14 is a colorless, viscous liquid (m.p.: 1°C; b.p.: 30°C (0.02 mbar)).



Metalation of the amide groups can be carried out with NaH in DMF, dimethyl sodium in DMSO, or potassium tert.-butylate in DMSO. Especially well suited polyamides are: polyamide 6, polyamide 66, and poly(trimethyl hexamethylene terephthal amide (Trogamid T)). For alkylation we utilized the following compounds: RX = benzyl chloride, p-chlorobenzyl chloride, alkyl chlorides as well as the homologous series of n-alkyl bromides $\text{CH}_3-(\text{CH}_2)_x-\text{Br}$ with $0 \leq x \leq 21$. Provided that certain conditions are observed, chain degradation is negligible.

The degree of alkylation depend upon the experimental conditions. It can be as high as 100%. Obviously, the properties of the polyamides are altered by the alkylation reaction. With increasing degree of alkylation the solubility in not very polar solvents (THF, dioxane, CHCl_3 , CH_2Cl_2) increases. Only partially alkylated polyamides may not be soluble enough. They can be converted to the N-trifluoroacetyl derivatives (19) by treatment with trifluoroacetic anhydride.



These materials are very well soluble in CH_2Cl_2 or CHCl_3 and can be characterized via GPC and NMR measurements (Ref. 32,33). Through these methods, the degree of alkylation can be determined quantitatively.

The N-alkyl polyamides exhibit remarkable thermal properties. With increasing degree of alkylation or with increasing length of the alkyl chain, the glass transition temperature is considerably decreased (Table 3). When the alkyl groups comprise more than 13 methylene units, the corresponding DSC trace exhibits endothermic first order phase transitions which can be interpreted in terms of side chain crystallinity. Melting points and melting enthalpies increase with increasing length of the side chains (Table 4) (Ref.34). It must be pointed out that due to their regular grafting points and the uniform branch length these polymers represent perfect "comb-like" copolymers (20).

Similar, regularly branched polymers are available by alkylation of linear polyethylene imine (Ref.35). Linear polyethyleneimine was synthesized according to the well-known method at Saegusa (Ref. 36) by ring-opening polymerization of 2-methyloxazoline. From the reaction with equivalent amounts of alkyl halogenides, the corresponding polymeric tertiary amines are obtained (21) ($x:\text{Br};\text{I};\text{R}:\text{C}_n\text{H}_{2n+1}$ with $n=2-18$). Quantitative yields can be achieved in alcoholic solution using alkyl bromide in the presence of K_2CO_3 and a little bit KI.

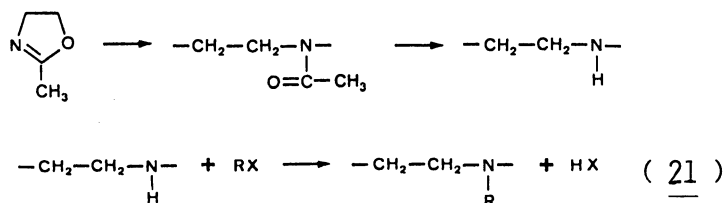


TABLE 3. Glass transition temperatures of N-alkylated Trogamid T

R	degree of substitution %	$T_g/^\circ\text{C}$	R	degree of substitution %	$T_g/^\circ\text{C}$
H	0	148	$n\text{-C}_3\text{H}_7$	100	48
	14	137	$n\text{-C}_4\text{H}_9$	100	35
"	70	99	$n\text{-C}_6\text{H}_{13}$	100	13
"	100	92	$n\text{-C}_8\text{H}_{17}$	100	-8
CH_3	100	69	$n\text{-C}_{10}\text{H}_{21}$	100	-25
$n\text{-C}_2\text{H}_5$	100	54			

TABLE 4. Crystalline melting points of totally N-alkylated Trogamid T

R	T_m $^\circ\text{C}$	
$n\text{-C}_{14}\text{H}_{29}$	-30	(20)
$n\text{-C}_{16}\text{H}_{33}$	17	
$n\text{-C}_{18}\text{H}_{37}$	34	
$n\text{-C}_{22}\text{H}_{45}$	50 (20)	

Also in the case of these regularly branched polymers the glass transition temperatures decrease with increasing length of the alkyl chain. Alkyl moieties carrying more than 10 carbon atoms, again bring about first-order phase transitions. The phase transition temperatures increase with increasing alkyl chain length; e.g. polytetradecyl ethyleneimine ($n=14$) has m.p. $+50^\circ\text{C}$, polyoctadecylethyleneimine ($n=18$) has m.p. $+75^\circ\text{C}$.

Poly-N-alkylethyleneimines form chelate complexes with transition metal salts as Cu(II), Ni(II), Co(II), Co(III), Pd(II), and Cr(III). These complexes are well soluble in organic solvents. The copper complexes are deep-green colored. With chloroformic solution of poly-N-alkylethyleneimine the ions can be extracted quantitatively out of an aqueous CuSO_4 solution.

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