Electrophilic aromatic substitution on poly-(4-N,N-dimethylaminostyrene-co-styrene) copolymers

Evidence for intramolecular hydrogen bonding

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Summary

Poly-[-4-(N,N-dimethylamino)styrene and its copolymers are prepared by standard radical polymerization proceeding and modified using 4-phenyl-1,2,4-triazoline-3,5-dione (PTD). From IR- and NMR-spectroscopy and the intrinsic viscosity [η] it can be deduced that hydrogen bonds mainly are formed between the dimethylamino group and the proton of the urazole ring, contrary to the formation of dimeric hydrogen bond complexes in modified polydienes. The basicity of the dimethylamino group is too small to abstract the urazole proton completely, which would generate a zwitterionic species.

Introduction

Intra- and intermolecular association strongly influences the dilute solution as well as the bulk properties of polymers. Polydienes modified with 1,2,4-triazoline-3,5-diones can form dimeric chelate-like hydrogen bond complexes/1,2/. These hydrogen bond complexes determine the polymer properties.
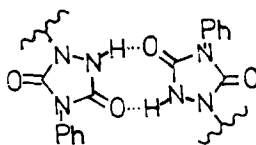

Dimeric hydrogen bond complexes between two urazole rings

In dilute solutions of modified polydienes a decrease of the intrinsic viscosity [η] compared to the unmodified polymer is observed/3-5/. In bulk a thermoreversible network is formed by hydrogen bonds. The viscoelastic properties of these networks previously have been described in detail/6-8/. The theoretical attempts to understand the association behaviour have been made/9/.

So far mainly polydienes were used as reaction partners for PTD. Recently G.B. Butler/10/ has shown that triazolinediones undergo a fast electrophilic substitution with electron rich aromatic compounds. Typical examples are poly-[-(N,N-dimethylamino)styrene (PDMAS), poly(2,4,6-trimethoxy)styrene (PTMS) and poly(N-methyl-2-vinylpyrrole) (PMVP).

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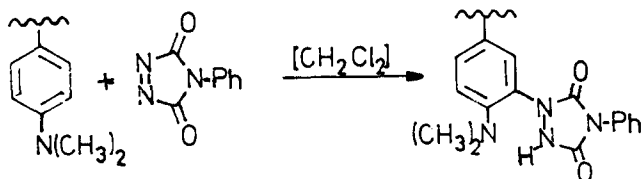
Substitution of PDMAS with PTD according to Butler /10/

It is the purpose of the present work to test whether the results obtained for polydienes might be extended to polymers with electron rich functional groups, i.e. whether a small number of functional polar groups will dramatically influence the properties of those electron rich aromatic polymers.

Additional interest might arise from the different basicity of the DMA-unit and the urazole group ($pK_a(H_2O)=5$). This might result in the formation of zwitterionic species.
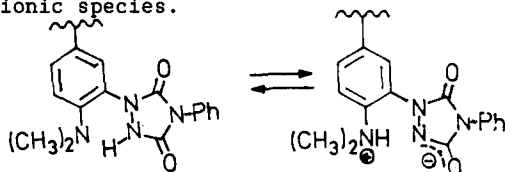
Schematic formation of zwitterionic species

Such a zwitterion formation is suggested by the acidity of the urazole group/11/ and the basicity of a dimethylamino group. Properties of other types of polyzwitterionic systems, based on poly-sulphopropylbetaines have been studied in detail by J.C. Galin et al/12-15/. As a general trend Galin and co-workers showed that the solubility in organic solvents is restricted to protic solvents with high dipole moments. Salt addition promotes water solubility of these polymeric zwitteriones. It is observed that the effect of salt addition is much higher in the lower concentration range and the intrinsic vicosity is increasing with salt concentration.

In the present paper the chemical modification of radically polymerized PDMAS and PDMAS-co-PS is presented. The observed behaviour of this materials is discussed with respect to the complex formation in these polar modified polymers.

Experimental

Characterization

4-N,N-Dimethylamino styrene (DMAS) was synthesized via Wittig reaction from the corresponding aldehyde, according to literature/10/. The copolymers were synthesized by radical copolymerization of DMAS and styrene. 9 g of the monomer mixture (Tab.1) and 158 mg AIBN were dissolved in 50 mL benzene in a glass tube. The reaction mixture was degased, sealed under high vacuum and placed into an oil bath at 75°C for 40h. The resulting

polymer was isolated by precipitation in 400 mL methanol. The solid polymer was collected, washed with additional methanol and dried under vacuum. The mole fraction of DMAS within the polymer was determined by quantitative NMR analysis.

Tab.1: *Synthesized polymers - yields and compositions*

	polymer	M_D	m_d	yield [g]	[%]	$[\eta]$ 1/g
1	PScoDMAS05	0.036	0.068	6.3	70.0	12.5
2	PScoDMAS10	0.073	0.105	3.8	42.2	12.2
3	PScoDMAS20	0.150	0.155	4.0	44.4	10.2
4	PScoDMAS40	0.321	0.388	3.4	37.7	10.4
5	PDMAS	1.000	1.000	5.8	64.4	8.7

M_D: mole fraction of DMAS in monomer mixture

m_d: mole fraction of DMAS in copolymer

Tab.2: *Conditions for the modification of polymers; degrees of substitution and intrinsic viscosities* $[\eta]$

sample	M_O	P (mmol)	PTD (mmol)	mol-% urazole	$[\eta]$ 1/g
PScoDMAS05-PTD05	106.84	9.36	0.47	5.0	12.0
PScoDMAS05-PTD02	106.84	9.38	0.14	1.5	-
PScoDMAS05-PTD01	106.84	9.37	0.07	0.7	-
PScoDMAS10-PTD05	108.21	9.25	0.45	4.9	9.1
PScoDMAS20-PTD05	111.05	9.01	0.45	5.0	9.5
PScoDMAS40-PTD05	120.68	8.28	0.41	5.0	8.7
PDMAS-PTD05	147.00	6.81	0.35	5.1	9.2
PDMAS-PTD10	147.00	6.80	0.69	10.1	-
PDMAS-PTD50	147.00	1.03	0.52	50.0	-
PDMAS-PTD02	147.00	6.81	0.19	2.8	-
PDMAS-PTD01	147.00	6.82	0.09	1.3	-
PDMAS-PTD100	147.00	0.68	0.68	100.0	-

M_O = average molar mass of repeating unit of the parent polymer

P   = amount of polymer (in mmole of repeating units) used in the modifcation

$[\eta]$ = intrinsic viscosity measured in toluene at 25^OC

mol-% = theoretical degree of modification

PTD   = amount of added PTD in mmol

Modification of Polymers

PTD was synthesized according to literature/17/ prescriptions. The electrophilic substitution of the polymers to the corresponding modified materials was performed at room temperature:
1 g of polymer was dissolved in 20 mL CH_2Cl_2 in a 50 mL flask. A solution of the corresponding amount of PTD (s. Tab.2) was added dropwise under vigorous stirring. The deep red solutions lost their color within a few seconds and turned to light orange. The mixture was stirred at room temperature for about one hour, then poured slowly into a beaker containing 300- 400 mL of petrol ether 40/80.

IR-spectrocopy: Spectra were run on a Bruker IFS-88 FT-IRspectrometer in the range between 400 cm^{-1} and 4000 cm^{-1}. A polymer film was cast from solution onto NaCl windows in appropriate thickness and 60 scans were taken for each spectrum with a spectral resolution of 4 cm^{-1}.
NMR-spectroscopy: The NMR-spectra were run on a 80 MHz Bruker spectrometer in a solution of $CDCl_3$.

Results

NMR-spectroscopy

Fig.1: _NMR-spectra of some polymers in the region between 2 ppm and 3 ppm._
a: PScoDMAS05 | PScoDMAS05-PTD05; b: PScoDMAS20 | PScoDMAS20-PTD05;
PDMAS | PDMAS-PTD50
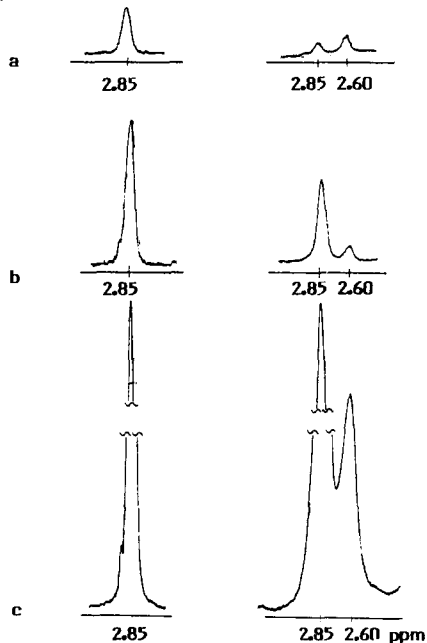
^{1}H-NMR-spectroscopy can be used to study the protonation of the DMA-group. Upon protonation of N,N-dimethylaniline a dublett signal at 3.4 ppm is observed, instead of the singulett signal near $\delta = 2.9$ ppm for dimethylaniline /16,17/. Hence we expect a similar shift of the dimethyl-amino protons of PDMAS, if a polymeric zwitterion is formed.

The aromatic resonances of the unmodified copolymers near $\delta = 7$ ppm are a simple superposition of the resonances of pure PDMAS and polystyrene /18,19/. The α and β-protons of the aliphatic protons give distin-guishable resonances centered at $\delta = 1.4$ ppm and $\delta = 1.8$ ppm. The most important signal for the following discussion arises from the dimethyl-amino protons at $\delta = 2.85$ ppm.

Tab.3: *Comparison of calculated and observed intensity ratio of the two signals of the DMA-groups of modified polymers*

	$\delta(CH_3')/\delta(CH_3)$	$\%[CH_3'_{th}]$	$\%[CH_3'_{exp}]$
PScoDMAS05-PTD-05	2.6/2.85	50.0%	55.6%
PScoDMAS10-PTD-05	2.6/2.85	25.0%	30.3%
PScoDMAS20-PTD-05	2.6/2.85	12.5%	19.2%
PScoDMAS40-PTD-05	2.6/2.85	6.3%	8.3%
PScoDMAS100-PTD-05	2.6/2.85	2.5%	2.3%
PDMAS-100-PTD-10	2.6/2.85	5.0%	9.9%
PDMAS-100-PTD-50	2.6/2.85	25.0%	29.4%
PDMAS-100-PTD-100	2.5/2.85	-	-

$\delta(CH_3')$: $\delta(ppm)$ of the methyl groups shifted to $\delta = 2.6ppm$

$\delta(CH_3)$: $\delta(ppm)$ of the unshifted methyl groups

$\%[CH_3'_{th}]$: theoretically expected fraction of the shifted methyl group (in %)

$\%[CH_3'_{exp}]$: observed fraction

NMR-spectra of the corresponding PTD-modified polymers show the phenyl group resonance at 7.5 ppm. The most significant difference is the split-ting of the DMA-resonance into two peaks. One of these two peaks is shif-ted to $\delta = 2.6$ ppm. The intensity ratio of these peaks depends on the degree of modification.

Under the assumption that only one methyl group of a modified DMAS-unit is shifted to higher field, the theoretical intensity ratio of the peaks belonging to the protons of the dimethylamino group can be calculated. Within the error limits of NMR-integration the experimentally determined intensity ratios are in agreement with theoretically calculated ones (Tab.3).

IR-spectroscopy

The analysis of the carbonyl vibration can be used to analyze the hydro-gen bond formation involving urazole groups. The IR-spectrum in this

region is governed by a strong absorption around 1720 cm^{-1}. The small absorptions near 1613 cm^{-1} (belonging to skeletal vibrations of the aromatic ring) and at 1770 cm^{-1} (attributed to symmetric C=O vibration of the urazole) will not be considered further. In a former investigation of PTDmodified polybutadienes the asymmetric vibrations at about 1703 cm^{-1} (complexed) and 1725 cm^{-1} (free) have been used to study the complexation behaviour.

Fig.2: *IR-spectra of in the carbonyl stretching region; a: PScoDMAS10-PTD05; b: PScoDMAS20-PTD-05; c: PDMAS-PTD50; d: PDMAS-PTD100*
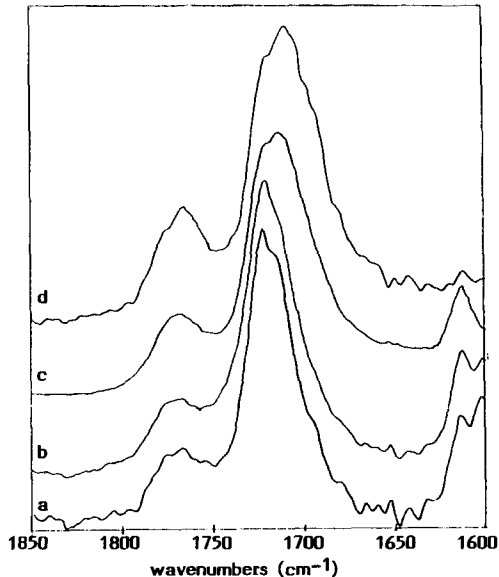

In comparison with the modified polybutadienes the following results must be noticed: The main absorption for all modified polymers occurs near 1722 cm^{-1}. With the exception of the 100%-modified PDMAS none of the modified polymers shows a shoulder at about 1700 cm^{-1}, which would indicate the presence of a urazole-urazole complex.

Discussion

As has been mentioned in the preceeding sections, a hydrogen transfer to the DMA-group should result in a shift of the NMR-signal of the DMA-protons to lower magnetic field. Contrary to this expectation we notice that one of the methyl groups in a modified DMAS-unit is shifted to higher field ($\delta = 2.6$ ppm). This result is in contradiction to the formation of a zwitterionic species. Obviously te acidity of the urazole group is not strong enough to transfer the proton to the DMAgroup. This is in agreement with the pK_a-values determined in mixtures of H_2O with organic solvents. With increasig amount of organic solvent the pK_a-values increase/11/.

A reasonable explanation of the observed behaviour can be given if the

formation of an intramolecular hydrogen bond between the urazole proton and the DMA-group is assumed.
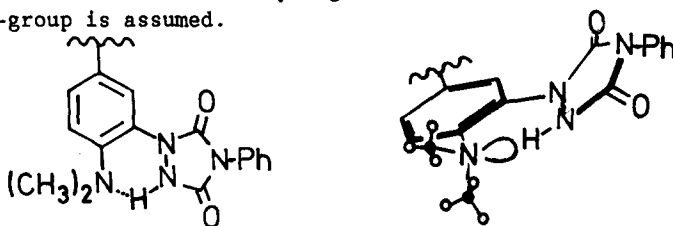
Formation of a hydrogen bond between the urazole proton and the DMA-group and spatial model

A three-dimensional model of a modified monomeric unit shows the different location of the two methyl groups with respect to the phenyl group. This implies a different local magnetic field induced by the ring-current effect of the phenyl group, and consequently a change in the chemical shift.

The formation of intramolecular hydrogen bonds is also evident from the IR-spectra.

For the modified PScoDMAS-samples no urazole-urazole complexes are formed besides the 100%-modified PDMAS where a shoulder at about 1703 cm^{-1} is an indication for a urazole-urazole complex formation.

Besides the absorption at 1722 cm^{-1} typical for free urazole groups an absorption at 1713 cm^{-1} is present in all of the modified samples, either as a shoulder or as a peak (see Fig.2). This absorption would be in agreement with the weaker hydrogen bond between the DMA-group and the urazole. Of course a hydrogen bond also might be formed between an urazole group and a DMA-group which is not substituted. In this case we would expect that dilute solution viscosity would strongly decrease in the presence of the urazole groups due to a partial coil collapse.

In the last row in the Tables 1 and 2 the intrinsic viscosities measured in toluene at 25°C are listed for the starting copolymers and some of the modified samples.

The decrease in [η] is within the experimental errors. These results show that hydrogen bond formation predominatly occurs between the urazole and the DMA-group of the same repeating unit (see spatial formula).

Acknowledgement

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