

Synthesis and Properties of Poly(acrylonitrile-*co*-*p*-trimethylsilylstyrene) and Poly(acrylonitrile-*co*-*p*-trimethylsilylstyrene-*co*-styrene)

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ABSTRACT: Copolymerization of acrylonitrile (AN) with *p*-trimethylsilylstyrene (TMSS) was carried out at 60°C in bulk and in solution in the presence of 2,2'-azobisisobutyronitrile (AIBN). The reactivity ratios of AN (M_1) and TMSS (M_2) were determined to be $r_1 = 0.068$ and $r_2 = 0.309$. The effects of the AIBN concentration and that of the chain transfer agent CCl_4 on the molecular weights (MWs) of the copolymers were investigated. An increase in the concentrations of AIBN or CCl_4 in solution led to a decrease in MW. Poly(AN-*co*-TMSS-*co*-St) was synthesized in solution using AIBN as the initiator. The molar fraction of AN was 0.415, while the molar ratio of TMSS/St varied from 1 : 1 to 1 : 9. The transition temperatures and thermal and thermooxidative stabilities of poly(AN-*co*-TMSS) and poly(AN-*co*-TMSS-*co*-St) were investigated. The differential scanning calorimeter technique was used to determine the compatibility of the poly(AN-*co*-TMSS) and poly(AN-*co*-TMSS-*co*-St) with commercial poly(AN-*co*-St). All the blends show a single glass transition temperature, which indicates the compatibility of the blend components. The surface film morphology of the blends mentioned above was examined by X-ray photoelectron spectroscopy. The data obtained indicate that the silicon-containing copolymer is concentrated in the surface layer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1920–1928, 2000

Key words: copolymerization; *p*-trimethylsilylstyrene; acrylonitrile; reactivity ratios; thermal analysis; compatibility; surface morphology

INTRODUCTION

In some cases the processing and exploitation of a polymers entails a problem that stems from the surface characteristics of the polymer blend. It might be expected that addition of low and high molecular surfactants that concentrate on the surface of polymer blends will effectively change

the surface characteristics of polymers (e.g., decrease the friction coefficient and the degree of the surface “roughness” due to the discontinuity of the supermolecular structures and related undesired sound effects that appear during exploitation of rubbing or contacting articles).^{1–3} Stable polymer compositions prepared by adding a small amount (0.1–5%) of polymers and copolymers, which are compatible with the basic polymer, have low surface energy and are concentrated in the surface layers owing to the different solubility parameters, may be particularly effective.^{4,5} Copolymers of fluoro- and silicon-containing mono-

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mers are the most effective surfactants.^{6,7} As a rule, the surface of the compositions modified by these substances is either enriched or composed of a fluoro- or silicon-containing component, and the surface characteristics of the composition material are determined for the most part by the properties of the modifying additive. Organosilicon modifiers of the surface properties of compositions reported to date are based on polysiloxanes. In the case of ABS plastics, however, the preparation of compatible copolymer modifiers based on polysiloxanes offers problems, because it is difficult to prepare copolymers with units of a related nature (styrene or acrylonitrile), which ensures the copolymer compatibility. Therefore, it was interesting to prepare modifiers on the basis of unsaturated hydrocarbons without the siloxane chain. Among these monomers, the group of silicon-substituted styrenes, which can readily undergo copolymerization with acrylonitrile (AN) or styrene (St) through the radical or ionic mechanism, attract particular attention. Silicon hydrocarbons are also of interest as comonomers because of a commercial availability of the starting organosilicon compounds, organochlorosilanes, for example, trimethylchlorosilane.

The goal of this work was to develop new modifiers for ABS plastics. To this end, we synthesized poly(AN-*co*-TMSS) and poly(AN-*co*-TMSS-*co*-St) and studied their properties.

EXPERIMENTAL

Materials

Commercial *p*-chlorostyrene and trimethylsilyl chloride (Aldrich Chemicals) were distilled before use. Monomer-*p*-trimethylsilylstyrene (TMSS) was synthesized, as described in Petrov et al.⁸ and was distilled under reduced pressure over CaH₂. Tetrahydrofuran (THF), benzene, toluene, AN, and St were purified by conventional methods. 2,2'-Azobisisobutyronitrile (AIBN) was refined by double recrystallization from methanol. The samples of copolymers AN with St : DN-52 (27 wt %, 42 mol % AN) and DN-77 (32 wt %, 48 mol % AN) were kindly provided Monsanto Corporate Research.

Instruments

Thermogravimetric analysis was carried out using a TG 50 thermal balance of TA 300 Mettler

TGA system in an atmosphere of N₂ or air at a flow rate of 0.3 10⁻⁵ m/s. Thermograms were obtained with a differential scanning calorimeter (DSC-30) of the TA-300 Mettler TGA system. The glass transition temperature was determined in the region of the abrupt change in the heat capacity with an accuracy of 10%. The rates of heating were 5 and 10°C/min, respectively. The DSC technique was used to determine the compatibility of the copolymer blends.

Average molecular weights (MWs) and the molecular weight distributions (MWD) were determined by gel permeation chromatography (GPC; Waters, Waters-401). THF was used as a solvent.

Contact angle measurements were made on a Ramey-Hart contact angle goniometer on copolymer films prepared by casting from a 2% (w/v) THF solution. Water (bidistillate) and glycerol having different surface tensions were used. The results were reproducible to within ±1° in most experiments.

The film surface was analyzed using X-ray photoelectron spectroscopy (XPS). The XPS spectra were taken on a Kratos Analytical Instruments XSAM-800 dual-chamber spectrometer equipped with a hemispherical electron energy analyzer and quad-anode X-ray source. The energy resolution of the spectrometer was 1.1 eV as determined on the Ag_{3d} core level using Mg K_α radiation.

Synthesis of Copolymers

Poly(AN-*co*-TMSS)

The copolymerization experiments were carried out in previously heated and evacuated glass ampules. The required amounts of AIBN, AN, TMSS, and solvent were placed in an ampule. Oxygen was removed from solution by vacuum degassing using the freeze-thaw technique. After the ampule was sealed off under high vacuum, the mixture was allowed to react at 60°C. When the reaction was complete, the ampule was opened and the reaction product was dissolved in toluene and precipitated into methanol. Each sample was precipitated two times. The precipitated copolymer was filtered off and dried at 30°C until a constant weight was achieved. The copolymer composition was determined by elemental analysis for Si and N.

RESULTS AND DISCUSSION

Copolymer Reactivity Ratios in AN-TMSS Copolymerization

To estimate the reactivity of TMSS in the copolymerization with AN, the reactivity ratios were

Table I Copolymerization of (AN-TMSS)

Acrylonitrile (mole fraction)		
Initial Mixture (M_1)	Copolymer (m_1)	Conversion (wt %)
0.107	0.224	4.00
0.208	0.323	6.25
0.310	0.378	6.20
0.450	0.422	15.00
0.528	0.450	8.20
0.686	0.510	12.80
0.820	0.564	12.44
0.901	0.629	12.39

$r_1 = 0.068 \pm 0.021$; $r_2 = 0.309 \pm 0.033$; Initiator-AIBN, $T = 60^\circ\text{C}$.

determined. For this purpose, the polymerizations of the initial monomer mixtures of various composition were carried out up to low degrees of conversions. The results are given in Table I. Using the data represented in Table I, the copolymerization parameters were calculated by the Kelen-Tudos method.^{9,10} The parameters of bulk copolymerization for a AN(M_1)-TMSS(M_2) pair were found to be $r_1 = 0.068 \pm 0.021$ and $r_2 = 0.309 \pm 0.033$. The values of the copolymerization parameters mean that poly(AN-co-TMSS), having an almost uniform composition, can be prepared, if the conversion of monomers does not exceed 60%. Figure 1 shows the theoretically expected AN molar fraction in copolymer as a function of the AN molar fraction in the monomer mixtures. The copolymer composition curve plotted in Figure 1 for the bulk copolymer crosses a diagonal at P ($m_1 = M_1 = 0.415$ molar fraction). At the point of intersection, the composition of the copolymer and the monomer feed are identical. For the monomer composition to the right of the cross-over point, AN will enter the copolymer composition more slowly than TMSS, while for monomer compositions to the left of P , the situation is the reverse.

Synthesis of Poly(AN-co-TMSS)

Synthesis of poly(AN-co-TMSS) was carried out at 60°C in bulk or in solution in the presence of AIBN. Copolymers of various MWs were prepared by changing the initiator concentration in the reaction mixture. Low molecular weight copolymers were synthesized in presence of the chain transfer agent, carbon tetrachloride (CCl_4). The comono-

mer concentration ratio corresponded to the azeotropic point (AN molar fraction = 0.415).

The conditions of copolymerization and the characteristics of poly(AN-co-TMSS) are given in Table II. We found that CCl_4 is the most effective agent for the regulation of MW of copolymers. Thus, in the bulk copolymerization, M_n of the copolymer decreased from 155×10^3 (run 94) to 26.8×10^3 (run 92) in presence of CCl_4 . Variation in the initiator concentration affects MW in a similar manner. Decreasing the AIBN concentration from 0.032 to 0.015 mol/L increased M_n from 33.6×10^3 (run.97) to 87.5×10^3 (run.99). The copolymerization experiments in runs 97–99 were carried out in toluene.

A decrease in the initiator concentration initiator, however, caused not only a growth of the copolymer MW (run.99), but also the MWD measured by GPC acquired a bimodal character due to the appearance of high molecular chains in the copolymer. The finding is likely associated with an increase in the medium viscosity and in the decreased probability of the chain termination (the gel effect) at high conversions. This phenomenon was eliminated by adding an inert diluent, benzene. The AIBN concentration in run 101 was almost the same as that in run 99, but benzene was added (the molar ratio benzene/toluene was $\sim 1/2$). The resulting copolymer (run 101) had a monomodal MWD, unlike copolymer produced in run 99. However, a decrease in the initiator con-

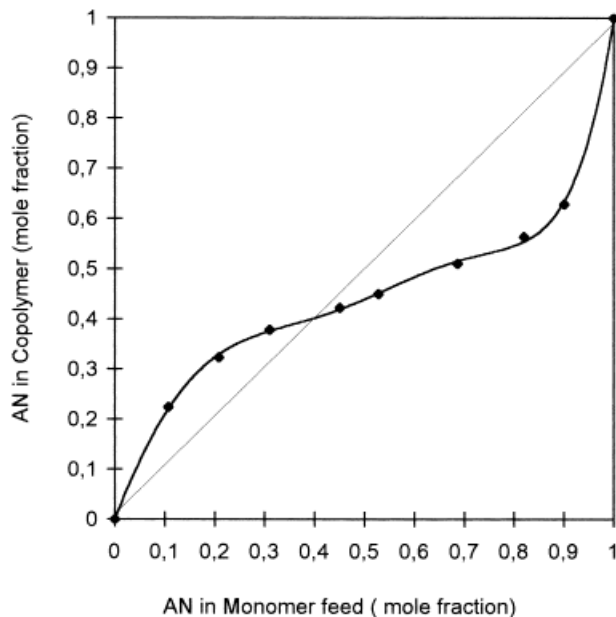
**Figure 1** Copolymer AN-TMSS composition curve.

Table II Synthesis Conditions and Molecular Characteristics of Poly(AN-co-TMSS)

Run No.	[AN] (mol/L)	[TMSS] (mol/L)	[AIBN] (mol/L)	[CCl ₄] (mol/L)	Time (h)	Yield (%)	TMSS in Copolymer (mol %)	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w/M_n
94	2.86	4.04	0.052	—	1.5	35.4	60.0	423	155	2.72b
92	1.43	2.02	0.025	5.18	10.0	81.2	58.5	72.3	26.8	2.70m
97	1.43	2.02	0.032	—	10.0	75.2	59.1	117	33.6	3.48m
98	1.43	2.02	0.015	—	10.0	67.1	60.0	166	51.0	3.25m
99	1.43	2.02	0.010	—	10.0	66.2	58.5	357	87.5	4.10b
101	1.02	1.44	0.009	—	13.0	61.8	60.0	188	55.0	3.40m
102	1.02	1.44	0.006	—	16.0	63.9	59.8	248	58.5	4.2b
104	0.95	1.34	0.007	—	15.0	67.1	57.8	171	54.0	3.17m
105	0.75	1.06	0.003	—	23.0	61.1	60.0	171	86.1	1.99m
109	0.75	1.06	0.002	—	30.0	59.4	57.0	248	122.1	2.04m
110	0.75	1.06	0.004	—	20.0	61.0	57.8	165	71.7	2.3m

AN, 41.5 mol %; p-TMSS, 58.5 mol %; $T = 60^\circ\text{C}$.

centration down to 0.006 mol/L (run 102) (the other conditions were analogous to those in run 101) yielded a copolymer with bimodal MWD. Therefore, the content of benzene in solution was increased so that molar ratio of benzene/toluene was $\sim 1/1.5$ (runs 104, 105, 109, 110). Under these conditions, copolymers having a monomodal MWD were obtained even at a very low concentration of the initiator: 0.002 mol/L (run 109). Thus, copolymers having an M_n ca. 50×10^3 were prepared in runs 104, 101, and 98 in the AIBN concentration range from 0.007 to 0.015 mol/L, and the total concentration of monomers ranged from 2.30 to 3.45 mol/L.

In order to keep the copolymer MW at the level of 70×10^3 to 120×10^3 , the concentration of the initiator was lowered to 0.004–0.002 mol/L. In this case, the monomodal character of MWD did not change, because copolymerization took place in a dilute solution ($C_{\text{AN}} = 0.75$ mol/L, $C_{\text{TMSS}} = 1.06$ mol/L) (runs 105, 109, and 110).

Thus, the conditions for the synthesis of poly(AN-co-TMSS) of the predetermined MW (from 30×10^3 to 120×10^3) with the monomodal MWD were determined.

Comonomer Composition and Rate of Copolymerization

The rate of copolymerization of AN with TMSS was studied as a function of the composition of the comonomer feed. The comonomers were polymerized in bulk in sealed ampoules at 60°C in the presence of 0.007 mol/L (0.1 mol % of total monomers) of AIBN initiator. The results obtained for

46/54 mol % and 90/10 mol % of the AN-TMSS comonomer composition are reported in Table III.

When AN-TMSS mixtures, containing more AN than the azeotropic composition, were copolymerized in bulk, the initial copolymers contained less AN than the initial feed. Thus, at low conversions of comonomers (15.0 and 26.3 wt %) polymerization of the comonomer mixture containing 46 mol % AN yielded copolymers consisting of 40.5 and 42.2 mol % AN, that is, the content of AN in copolymers was lower than in the initial feed (Table III). Analogous data were obtained in the copolymerization of AN-TMSS mixture containing 90 mol % AN. Copolymers obtained with a low yield (12.4 and 21.2 wt %) contained 62.9 and 64.4 mol % AN, that is, the content of AN was lower than in the initial monomer mixture (Table III).

Table III Rate of AN-TMSS Polymerization

No.	AN (M_1) in Monomer (mol %)	Time (h)	Yield (%)	AN (m_1) in Copolymer (mol %)
1	46	1.5	15.0	40.5
2	46	2.5	26.3	42.2
3	46	3.5	38.5	45.4
4	46	5.0	56.3	45.4
5	46	8.0	90.0	45.4
1	90	1.0	12.4	62.9
2	90	2.0	21.1	64.4
3	90	3.0	32.3	66.1
4	90	4.0	50.9	75.4
5	90	5.5	84.0	84.4

Initiator: AIBN; $T = 60^\circ\text{C}$.

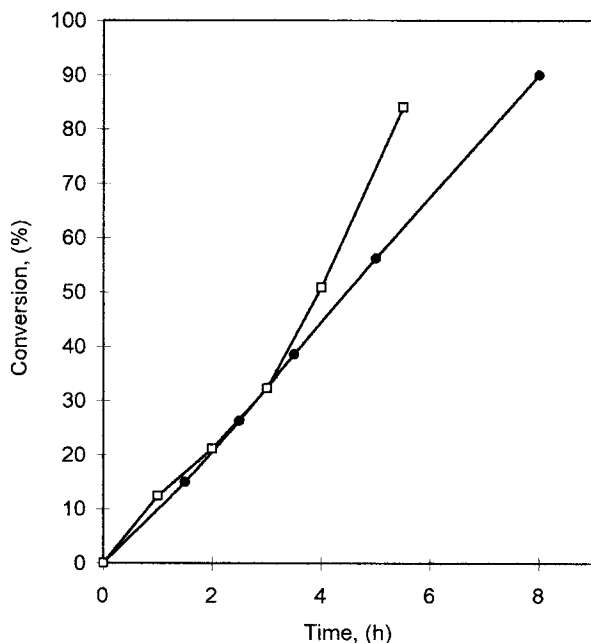


Figure 2 Bulk copolymerization AN with TMSS. ●, 46 mole % AN; □, 90 mole % AN, 0.1 mol % AIBN; temperature, 60°C.

During copolymerization, TMSS entered the copolymer at a faster rate as compared to AN; consequently, the residual monomer became enriched in AN.

The resulting copolymer represents a mixture of macromolecules having a wide range of chemical composition. The samples of poly(AN-co-TMSS) obtained up to 60% conversion were prepared for physical study. These copolymers had fairly uniform composition and showed solubility in toluene. Figure 2 shows the plots of percent conversion versus the time of polymerization. Curves 1 and 2 correspond to the different concentrations of AN in the initial monomer mixtures, 46 and 90 mol %, respectively. The initiator concentration was 0.1 mol % of the total concentration of monomers.

The curves given in Figure 2 show that the composition of the monomer mixture has almost no effect on the rate of polymerization up to the

40% conversion. Only at a high concentration of AN (90 mol %) in the initial monomer mixture does a noticeable increase in the polymerization rate take place at conversions above 40%. The remarkable acceleration of AN-TMSS copolymerization is due to two distinct factors: an increased viscosity ("gel effect") and variation in the comonomer composition with conversion (increasing the concentration of AN in the monomer mixture).

Synthesis of Poly(AN-co-TMSS-co-St)

In this case, previously reported data^{11,12} on the reactivity ratios and on the azeotropic point for the AN-St and St-TMSS comonomers and data on the copolymerization of AN with TMSS were used (Table IV). It is seen that the relative reactivity of St and TMSS are close to each other and to AN. Reasoning from this knowledge, we infer that the copolymerization of the ternary AN-TMSS-St mixture shows the same regularities as the copolymerization of AN-TMSS and AN-St mixtures.

Copolymerization was carried out under the same conditions as described in the copolymerization of AN with TMSS. The composition of the monomer mixture was consistent with the azeotropic point (0.415 molar fraction of AN). The molar ratio of TMSS : St in the starting monomer mixture changed from 1 : 1 to 1 : 9. The copolymer composition was determined using elemental analysis for Si and N. As a result, terpolymers containing ca. 40–60 mol % of AN and (1 : 1–1 : 10) units TMSS and St were obtained. The experimental data are given in Table V.

Investigation of the Temperature Transitions of Poly(AN-co-TMSS) and Poly(AN-co-TMSS-co-St): Thermal and Thermooxidative Stability of Copolymers

The results from DSC measurements of poly(AN-co-TMSS) and poly(AN-co-TMSS-co-St), as well as of polyTMSS and the commercial poly(AN-co-St) (DN-77, 32 wt % AN), are given in Table VI. As

Table IV Reactivity Ratios

M_1	M_2	r_1	r_2	T (°C)	Ref.
Acrylonitrile	Styrene	0.04	0.41	60	11
Acrylonitrile	<i>p</i> -Trimethylsilylstyrene	0.06	0.31	60	This work
Styrene	<i>p</i> -Trimethylsilylstyrene	1.00	1.00	70	12

Table V Synthesis Conditions and Molecular Characteristics of Poly(AN-*co*-TMSS-*co*-St)

Run No.	[AN] (mol/L)	[TMSS], (mol/L)	[St], (mol/L)	[TMSS/St], (mol/mol)		Time (h)	Yield (%)	Copolymer (mol %)			[TMSS/St] (mol/mol) Copolymer	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w/M_n
				Mon.	Mixt.			AN	TMSS	ST				
123	0.89	0.63	0.63	1 : 1		21.0	56.8	39.0	26.7	34.3	1 : 1.3	101.5	50.2	2.02
126	0.98	0.28	1.12	1 : 4		24.0	61.0	39.8	10.9	49.3	1 : 4.5	116.4	58.2	2.00
128	1.06	0.15	1.35	1 : 9		24.0	60.6	39.8	5.7	54.5	1 : 9.56	114.7	50.4	2.27
129	0.97	0.46	0.92	1 : 2		21.0	58.5	41.1	16.3	42.6	1 : 2.61	124.8	70.8	1.76

Solvent: toluene; Initiator: [AIBN]; $T = 60^\circ\text{C}$.

is seen, the thermal and thermooxidative stabilities of all of copolymers obtained from AN and TMSS are similar and close to the thermal characteristics of the commercial DN-77 copolymer.

All the copolymers studied exhibit a single relaxation transition temperature, which can be interpreted as the temperature of transition to the rubbery state (T_g). This confirms that the resulting copolymers have statistical chain distributions.

The T_g values were determined by the content of the silicon-containing comonomer, which homopolymer shows a T_g of 135°C . It varies from 130°C , for the copolymer prepared at the azeotropic point having 58.5 mol % of TMSS, to 115°C for poly(AN-*co*-TMSS-*co*-St), containing 5.7 mol % of TMSS, but remains higher than T_g for DN-77 ($T_g = 104^\circ\text{C}$).

Study of Compatibility of the Mixtures of the Silicon-Containing Copolymers with the Commercial Poly(AN-*co*-St)

The DSC technique was used to determine the compatibility of the copolymer blends. The pres-

ence of the single transition temperature, which is usually intermediate between the T_g values of the blend components, is indicative of compatible blends. The blends of poly(AN-*co*-TMSS) and poly(AN-*co*-St) were prepared from the combined solutions in methyl-ethyl-ketone. The DSC tests were carried out using films cast from these solution. The films were cast on a glass support, dried at room temperature, and then were heated in vacuum at 50°C to a constant weight and then for 3 h at a temperature higher than T_g of the starting components (140°C).

Table VII presents the relevant data. The mixtures containing 5 and 15 wt % of poly(AN-*co*-TMSS) show single glass transition temperatures, which do not change during repeated scanning. Therefore, we believe that the samples of copolymers prepared from solution are compatible. In order to get a more rigorous verification of the copolymer compatibility, similar tests were made for a mixture containing equal amounts of components (50 : 50). In this case the samples of blends heated at temperatures higher 140°C also show the single T_g . Its value is close to that cal-

Table VI Data of Thermal Analysis for Poly(AN-*co*-TMSS) and Poly(AN-*co*-TMSS-*co*-St)

Run No.	Copolymer (mol %)			TGA ^a									DSC T_g ($^\circ\text{C}$)
				Air			N ₂						
				TMSS	AN	ST	5%	10%	50%	Max. Speed	5%	10%	
88	100	—	—	305	315	345	347	322	336	374	384	135	
98	60.0	40.0	—	328	347	370	373	346	361	389	393	130	
113	40.0	60.0	—	335	349	377	382	349	360	387	390	127	
123	26.7	39.0	34.3	328	343	376	377	341	357	390	396	124	
128	5.7	39.8	54.5	332	346	378	382	347	361	392	397	115	
129	16.3	41.1	42.6	334	346	375	376	345	357	391	396	121	
DN-77	—	48.0	52.0	334	348	379	379	348	361	387	390	104	

^a Values are temperature in $^\circ\text{C}$.

Table VII DSC of Poly(AN-co-TMSS) with DN-77 Mixtures

Run	Poly(AN-co-TMSS) AN, mol %	Poly(AN-co-TMSS) in Mixture (wt %)	Scanning No.	T_g (°C)
110	42.2	5	1	105
			2	105
		15	1	105
			2	105
114	63.0	5	1	105
			2	105
		15	1	103
			2	105
104	42.2	50 After 2 months	1	114.5
				114.0

culated according to the Fox equation for a compatible copolymers.¹³ The film structure made from the copolymer blend (50 : 50) is stable thermodynamically. This conclusion is supported by the reproducibility of thermograms obtained after 2-month storage of the copolymer.

XPS Measurement

XPS provides an opportunity to obtain quantitative data about the surface composition. The surface morphology of a number of films of poly(AN-co-St) (DN-52, 27 wt % AN; DN-77, 32 wt % AN), poly(AN-co-TMSS) (16.5 wt % AN) and their mixtures (Table VIII, runs 4, 5, 6, and 7) was studied by XPS. In addition to experimental data on the elemental composition of the sample surface, Table VIII shows the calculated (theoretical) data for the elemental composition of the copolymers and their blends (at.%). Calculation was performed taking into account the molar fractions of AN and St (or TMSS) in the copolymer. To compare the experimental data on the elemental composition of the sample surface (XPS) with the calculated results, we took into consideration all the atoms involved in the copolymer, except for hydrogen.

As follows from Table VIII, for poly(AN-co-TMSS) (sample 3), the calculated amount of Si (6.82 at.%) virtually corresponds to its content at the surface (7.42 at.%). This fact provides evidence that the sample is homogenous with respect to composition.

Blends of poly(AN-co-St) and poly(AN-co-TMSS) (samples 4–7) have heterogeneous composition. The content of Si on the sample surface is appreciably higher than its calculated value. For exam-

ple, sample 6 prepared from a poly(AN-co-St) (DN-77, 48 mol % AN) and poly(AN-co-TMSS) blend and containing 5 wt % of organosilicon-containing polymer contains 2.62 at.% Si on the surface, while the calculated amount should be 0.48 at.% Si.

An increase in the content of poly(AN-co-TMSS) in the blend to 15 wt % (sample 7) leads to a rise in the content of Si on the sample surface to 4.64 at.% compared to 1.39 at.% which was calculated from the blend composition.

Analogous data were obtained for the poly(AN-co-TMSS) blends with poly(AN-co-St) (DN-52, 42 mol % AN; samples 4 and 5).

The data presented above indicate that the surface of film cast from the copolymer blends is enriched with the copolymer containing organosilicon component.

Contact Angle Measurement

The surface energy (γ) was calculated according to Wu¹⁴ from experimental values of the contact angles of wettability (θ) for two liquids: water and glycerol. The results obtained are shown in Table IX. It is seen that the highest surface energy (21.16 mJ/m²) is observed for poly(AN-co-St), while (18.15 mJ/m²) poly(AN-co-TMSS) has the lowest value. This is related to the presence of a (CH₃)₃Si group in the copolymer. Addition of poly(AN-co-TMSS) (15%) in poly(AN-co-St) decreases the surface energy down to 19.52 mJ/m². It is possible to assume that this will lead to a decrease in the friction coefficient of poly(AN-co-St).

Table VIII XPS Data for the Analysis of Copolymer Blends

Composition of Blends of Poly(AN- <i>co</i> -St) (DN-52, DN-77) with Poly(AN- <i>co</i> -TMSS), wt %			
Sample	DN-52 AN (42 mol %)	DN-77 AN (48 mol %)	Poly(AN- <i>co</i> -TMSS) AN (40 mol %)
1	100	—	—
2	—	100	—
3	—	—	100
4	95	—	5
5	85	—	15
6	—	95	5
7	—	85	15

XPS Data for the Analysis of Copolymer Blends

Relative Atomic Concentration (%) (Experiment)							
Element	Samples: 1	2	3	4	5	6	7
C, 1s	93.61	89.90	87.48	89.36	85.28	88.06	85.69
O, 1s	0.72	2.59	0.98	2.25	3.03	3.50	4.40
N, 1s	5.67	7.24	4.12	4.15	4.12	5.82	5.27
Si, 2s	—	—	7.42	4.24	7.57	2.62	4.64

Calculated Relative Atomic Concentration (%)							
Element	Samples: 1	2	3	4	5	6	7
C	93.33	92.10	88.64	93.01	92.38	91.86	91.40
N	6.67	7.90	4.54	6.52	6.28	7.66	7.21
Si	—	—	6.82	0.47	1.34	0.48	1.39

CONCLUSIONS

Two kinds of random copolymers, poly(AN-*co*-TMSS) and poly(AN-*co*-TMSS-*co*-St) were synthesized in bulk and in solution in the presence of AIBN. The reactivity ratios of AN(M_1) and

TMSS(M_2) were determined to be $r_1 = 0.068$, $r_2 = 0.309$.

The thermal stabilities of the silicon-containing copolymers are higher than that of poly(AN-*co*-St), because the T_g of poly-TMSS (135°C) is higher than that of polystyrene (104°C).

The AN-TMSS copolymers are compatible with the commercial poly(AN-*co*-St), their blends are stable with time, which allows their prolonged use.

The surfaces of the films prepared from the blends of silicon-containing copolymers and poly(AN-*co*-St) are enriched by the organosilicon component. This brings a decrease in the surface energy. Therefore, it is possible to assume that the friction coefficient of blends, containing poly(AN-*co*-TMSS), will decrease.

The copolymers synthesized show promise as compositional components with commercial AN-St plastics to modify their surface properties.

Table IX Contact Angle of Wettability (θ°) and Surface Energy (γ) for Different Copolymers

Copolymers	θ°		γ (mJ/m ²)
	Water	Glycerol	
Poly(AN- <i>co</i> -St) (DN-77)	94	83	21.16
Poly(AN- <i>co</i> -TMSS) (40 mol % AN)	93	86	18.15
DN-77 + 15% Poly(AN- <i>co</i> -TMSS)	95	85	19.52

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