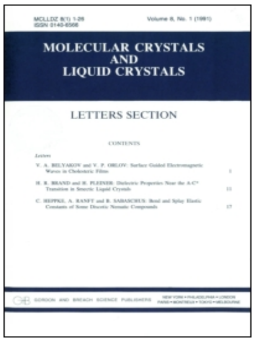

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: O. Manchenko, N. Iukhymenko & V. Nizhnik (2016) Chemical plasticizing of polyacrylonitrile by copolymerization with other monomers, Molecular Crystals and Liquid Crystals, 640:1, 98-105, DOI: 10.1080/15421406.2016.1255521

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1255521

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 640, 98–105
http://dx.doi.org/10.1080/15421406.2016.1255521

Chemical plasticizing of polyacrylonitrile by copolymerization with other monomers

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ABSTRACT
Chemical plasticizing of polyacrylonitrile (PAN) was carried out by copolymerization of acrylonitrile with other monomers such as methacrylic esters: vinyl acetate, vinyl benzoate, styrene, and butyl vinyl ether. We identified and analyzed parameters of PAN, polymer modifiers and their macromolecules as polymethyl methacrylate (PMMA), polybutyl methacrylate (PBMA), polyvinyl acetate (PVA), polyvinyl benzoate (PVB), polystyrene (PS), and polyvinyl butyl ether (PVBE).

This article reports the method of chemical plasticizing of polar chain polymer (PAN) by the reduction of polar parts and tuning the dipole moment value of the copolymer links.

KEYWORDS
copolymerization; methacrylic esters; polymer modifiers; polyacrylonitrile; chemical plasticizing

Introduction

The phenomenon of plasticization can be caused by the changes in the chemical composition of macromolecular chains during polymerization or during other polymer transformation processes. This kind of plasticization is called a chemical one. The main criterion of the chemical plasticization efficiency is the degree reduction of the polymer glass transition temperature (T_g). For those polymers that are in a glassy state the plasticization can also be revealed by the cohesive energy (E_{coh}) reduction, decrease of modulus of elasticity in shear (G_a) or tension or the reduction of dipole-segmental motion temperature ($T_{tg\delta max}$).

According to the literature data, it is believed that the cause of the chemical plasticization is the increase of kinetic flexibility of polymer chains by reducing the potential barrier of molecular units' rotation due to changes in intramolecular interactions [1]. However, it remains unclear how polymer parameters change depending on the stiffness of the polymer chain that is determined by the presence of side groups of different chemical composition.

It was investigated the chemical plasticization of the stiff chain polymer polyacrylonitrile (PAN), the particular properties of which are caused by the significant intermolecular electrostatic forces that come from the presence in its composition such fragments as –CN group with 0.5D dipole moment.

Chemical plasticizing of polyacrylonitrile (PAN) was carried out by copolymerization of acrylonitrile with other monomers: methacrylic esters (methyl methacrylate (MMA), butyl methacrylate (BMA), vinyl acetate (VA), vinyl benzoate (VB), styrene (St), and butyl vinyl

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ether (BVE)). We have determined and compared parameters of polyacrylonitrile (PAN), polymer modifiers and their macromolecules as polymethyl methacrylate (PMMA), polybutyl methacrylate (PBMA), polyvinyl acetate (PVA), polyvinyl benzoate (PVB), polystyrene (PS), and polyvinyl butyl ether (PVBE).

Copolymers were synthesized by radical polymerization of a mixture of appropriate monomers. As the initiator azobisisobutyronitrile (AIBN) was used in the amount of 1%. The composition of copolymers was determined analytically by nitrogen content.

Experimental

In physical and chemical experiments there were investigated polymer films (their thickness was 2-3 $\cdot 10^{-2}$ cm) that were obtained by compression at temperatures higher by 30°C rather than the fluidity temperature of those polymers; the pressure was 15 MPa and the compression was followed by cooling at a speed of 1 deg/min. The glass transition temperature of polymers was determined by two methods: thermomechanical method [2] (the temperature is indicated as T_g) and dielectric method (the temperature is indicated as $T_{tg\delta max}$). Thermomechanical curves were determined in conditions of constantly operating mechanical stress value of 0.85 MPa. The heating rate was 2 deg/min. The determination of dielectric characteristics ($T_{tg\delta max}$) was performed at a frequency of 700 Hz in the temperature range of 293 – 423K.

Density was determined experimentally by changing the concentration of potassium iodide with distilled water to equalize the density of the sample solution and the polymer.

Van der Waals volume of polymer molecules that is limited by electron clouds, and assigned to the monomer units (V_w) was calculated according to [3] using the formula:

$V_{mol}/V_w = 1.55$, where V_{mol} - molar volume of the polymer in the glassy state, referred to the monomer units $V_{mol} = M/\rho$ (M - molecular mass of structural units, ρ - polymer density).

Cohesive energy (E_{coh}) was calculated according to [3].

Shear modulus of the polymer in the amorphous state, or its stiffness (G_a) was calculated with the help of Van Krevelen and Hovtytsera empirical correlation.

$$G_a \approx \frac{3}{1+\frac{600}{T_C}} 10^9,\ H/m^2$$

Molar attraction constant (F) was calculated according to the following formula:

$$F = E_{coh} \cdot V_{mol} \cdot (298K)^{1/2}$$

The dipole moment of structural units (μ_{ef}) of macromolecules of original and annealed films was calculated by the Debye equation at 298 K: [3]

$$\left[\frac{\varepsilon-1}{\varepsilon+1}-\frac{n^2-1}{n^2+1}\right]\frac{M}{\rho}=\frac{4}{9}\pi N_a\frac{\mu_{ef}^2}{kT}\approx 20,6\mu_{ef}^2,$$

where ε - relative permittivity of conductive polymers, n - refractive index.

Results and discussion

It is shown that the possible method of chemical plasticization of stiff chain polymer PAN is to reduce the number of its polar structural units and the average dipole moment of the structural units of the copolymer. Nonpolar polystyrene in copolymers AN-St decreases the

Table 1. Parameters of PAN, PS and their copolymers.

		AN: St				
Parameters	PS	3:7	1:1	7:3	4:1	PAN
ε (298 K)[a]	2.55	2.71	2.8	2,93	2.99	3.10
$tg\delta_{max}\cdot 10^{2}$[b]	—	—	9.04	15,8	20.8	—
$T_{tg\delta max}$[c]	—	—	382	377	373	—
$\rho.10^{-3}$, kg/m^{3}[d]	1.048	1.088	1.116	1.143	1.156	1.184
E_{coh}, kJ/mol[e]	29.4	28.7	28.3	27.9	27.6	27.2
μ_{ef}, D[f]	0.17	0.27	0.34	0.41	0.44	0.51
F[g]	54.0	48.7	45.1	41.3	39.2	34.9
$V_{mol}\cdot 10^{6}$, m^{3}/mol[h]	99.2	82.8	72.0	61.1	55.7	44.8
T_{g}, K[j]	373	374	375	376	377	378
$V_{w}\cdot 10^{5}$, m^{3}/mol[i]	15.4	12.8	11.2	9.4	8.6	6.9
e_{coh}, kJ/m^{3}[k]	0.30	0.35	0.39	0.46	0.49	0.61
$G_{a}\cdot 10^{-9}$, N/m^{2}[l]	1.14	1.15	1.15	1.16	1.16	1.16

[a] relative permittivity of polymer
[b] dielectric loss tangent (dissipation factor)
[c] glass transition temperature (dielectric measurements)
[d] polymer density
[e] Molar cohesive energy
[f] dipole moment of structural unit (monomer link)
[g] Molar attraction constant
[h] molar volume of the polymer in the glassy state
[i] glass transition temperature (thermomechanical method)
[j] Van der Waals volume of structural (monomer) unit
[k] cohesive energy density
[l] Shear modulus of the polymer in the amorphous state (rigidity)

polarity of macromolecules (see Table 1), but the significant effect of this polymer plasticization is not achieved. Polystyrene units (PS) in macromolecules have a considerable size and mass of the side group that is attached firmly to the main chain with the considerable energy level of 388 kJ/mol. Conformational conversion of the chain that has these side groups in its structure requires considerable energy and causes significant inhibition of internal rotation of structural units. Therefore, despite a significant decrease of the average dipole moment, density, molar volume, cohesion energy in copolymers, the effect of chemical plasticizing of PAN by polystyrene is low; the glass transition temperature shift is only few degrees.

Conformational conversion of chain that has side groups can be easily facilitated when the side group is attached to the main chain through an oxygen atom in PVB, PVA, PVBE. The side group is very mobile, due to the small size of the Van der Waals radius of oxygen ($\sim 1{,}5\cdot 10^{-10}$m). The introduction of such structural units in the PAN polymer results in a significant reduction in temperature T_g, $T_{tg\delta\ max,}$ decrease of e_{coh} and G_a value despite the higher values of μ_{ef} in the PVA and PVB. Because of the larger side groups size in comparison with the -CN group of PAN polymer the value of V_{mol} and V_w is increased. For these polymers the chemical plasticizing effect depends on the size of radical that is bound to the oxygen atom; the increase of radical size reduces this effect. According to the plasticizing effect on the PAN chain, these polymers can be arranged in such series: PVBE> PVA> PVB (See Table 2, 3) [4].

When dipoles are not directly connected to the main chain (esters of methacrylic acid), the orientation of the dipole moments also occurs independently of changes in the shape of the macromolecule. However, the inertia of dipole rotation of these ethers is more than in PVA because of C-C bonds between the main chain and the side group. In these polymers the mobility of macromolecules is defined by persistent bonds between chains that are formed

Table 2. Parameters of PAN, PVBE and their copolymers.

Parameters	PVBE	AN:VBE				PAN
		2:1	1:1	1:2	1:3	
ε (298 K)[a]	2.34	2.85	2.72	2.59	2.53	3.10
tg $\delta_{max} \cdot 10^2$[b]	—	17.2	13.6	10.1	8,3	—
$T_{tg\delta\ max}$[c]	—	344	320	296	284	—
$\rho.10^{-3}$,kg/m^3[d]	0.923	1.097	1.050	1.010	0.988	1.184
E_{coh}, kJ/mol[e]	6.4	20.7	16.8	13.3	11.6	27.2
μ_{ef}, D[f]	0.41	0.48	0.46	0.44	0.43	0.51
F[g]	26.2	36.9	35.7	33.9	32.6	34.9
$V_{mol} \cdot 10^6$, m^3/mol[h]	107.5	65.7	76.1	86.6	91.8	44.8
T_g, K[i]	223	326	300	275	261	378
$V_w 10^5$, m^3/mol[j]	16.6	10.2	11.8	13.4	14.2	6.9
e_{coh}, kJ/m^3[k]	0.06	0.31	0.22	0.15	0.13	0.61
$G_a \cdot 10^{-9}$, N/m^2[l]	0.80	1.07	1.00	0.94	0.90	1.16

[a] relative permittivity of polymer
[b] dielectric loss tangent (dissipation factor)
[c] glass transition temperature (dielectric measurements)
[d] polymer density
[e] Molar cohesive energy
[f] dipole moment of structural unit (monomer link)
[g] Molar attraction constant
[h] molar volume of the polymer in the glassy state
[i] glass transition temperature (thermomechanical method)
[j] Van der Waals volume of structural (monomer) unit
[k] cohesive energy density
[l] Shear modulus of the polymer in the amorphous state (rigidity)

Table 3. Parameters of PAN, PVA, PVB and their copolymers.

Parameters	PVA	VA:AN		PAN	AN:VB				PVB
		1:1	1:3		2:1	1:1	1:2	1:3	
ε (298 K)[a]	3.22	3.16	3.13	3.1	3.03	3.0	2.97	2.95	2.9
tg $\delta_{max} \cdot 10^2$[b]	16.6	20.3	22.15	—	17.2	13.6	10.1	8.3	3.2
$T_{tg\ \delta max}$[c]	311	351	371	—	379	373	367	364	355
$\rho.10^{-3}$, kg/m^3[d]	1.19	1.187	1.185	1.184	1.14	1.12	1.09	1.08	1.052
E_{coh}, kJ/mol[e]	27.6	27.4	27.3	27.2	32.9	35.8	38.6	40.1	44.4
μ_{ef}, D [f]	0.65	0.58	0.54	0.51	0.56	0.59	0.62	0.63	0.67
F[g]	44.6	40.1	37.5	34.9	47.3	53.5	59.5	62.4	71.4
V_{mol} $10^{6,}$ m^3/mol[h]	72.2	58.5	51.6	44.8	68.2	79.9	91.6	97.4	115
T_g, K[i]	301	339	359	378	366	359	353	350	341
$V_w \cdot 10^5$, m^3/mol[j]	11.2	9.05	7.90	6.90	10.6	12.4	14.2	15.1	17.8
e_{coh}, kJ/m^3[k]	0.38	0.47	0.53	0.61	0.48	0.45	0.42	0.41	0.39
$G_a \cdot 10^{-9}$, N/m^2[l]	1.00	1.08	1.12	1.16	1.14	1.12	1.11	1.10	1.08

[a] relative permittivity of polymer
[b] dielectric loss tangent (dissipation factor)
[c] glass transition temperature (dielectric measurements)
[d] polymer density
[e] Molar cohesive energy
[f] dipole moment of structural unit (monomer link)
[g] Molar attraction constant
[h] molar volume of the polymer in the glassy state
[i] glass transition temperature (thermomechanical method)
[j] Van der Waals volume of structural (monomer) unit
[k] cohesive energy density
[l] Shear modulus of the polymer in the amorphous state (rigidity)

Table 4. Parameters of PAN, PMMA, PBMA and their copolymers.

		MMA:AN			AN:BMA				
Parameters	PMMA	1:1	1:3	PAN	2:1	1:1	1:2	1:3	PBMA
ε (298 K)[a]	3.15	3.14	3.12	3.1	3.07	3.04	3.03	3.01	2.9
tg $\delta_{max}{\cdot}10^2$[b]	4.6	12.3	15.5	—	22	18.2	13.7.	13.2	8.0
$T_{tg\delta\ max}$[c]	383	387	389	—	367	356	344	338	321
$\rho.10^{-3}$, kg/m^3[d]	1.17	1.179	1.182	1.184	1.059	1.061	1.062	1.102	1.052
E_{coh}, kJ/mol[e]	29.0	28.2	27.6	27.2	32.3	34.9	36.1	38.5	42.7
μ_{ef}, D[f]	0.65	0.61	0.59	0.51	0.58	0,60	0.62	0.63	0.65
F[g]	50.1	44.8	37.3	34.9	44.8	56,4	60.1	70.3	75.8
V_{mol} 10^6, m^3/mol[h]	86.5	65.6	56.1	44.8	74.8	89.9	104.8	112.4	135
T_g, K[i]	378	378	378	378	358	344	332	325	310
$V_w{\cdot}10^5$, m^3/mol[j]	13.4	10.2	8.7	6.9	11.6	13.9	16.3	17.4	20.9
e_{coh}, kJ/m^3[k]	0.33	0.42	0.49	0.61	0.43	0.38	0.34	0.33	0.31
$G_a{\cdot}10^{-9,}$ N/m^2[l]	1.16	1.16	1.16	1.16	1.12	1.09	1.06	1.05	1.02

[a] relative permittivity of polymer
[b] dielectric loss tangent (dissipation factor)
[c] glass transition temperature (dielectric measurements)
[d] polymer density
[e] Molar cohesive energy
[f] dipole moment of structural unit (monomer link)
[g] Molar attraction constant
[h] molar volume of the polymer in the glassy state
[i] glass transition temperature (thermomechanical method)
[j] Van der Waals volume of structural (monomer) unit
[k] cohesive energy density
[l] Shear modulus of the polymer in the amorphous state (rigidity)

by polar substituents and by the radical size of the side group. In PMMA due to the small size of radical dominates the effect of chain-chain bonds that inhibit the internal rotation. Therefore, in case of chemical plasticizing of PAN by methyl methacrylate at the temperature (T_g, $T_{tg\delta max}$) the modulus of elasticity in shear is changed slightly. The cohesive energy density is also reduced slightly because of the increase of the molar and Van der Waals volume of structural units.

In these polymers the mobility of macromolecules is defined by persistent bonds between chains that are formed by polar substituents and by the radical size of the side group. In PMMA due to the small size of radical dominates the effect of chain-chain bonds that inhibit the internal rotation. Therefore, in case of chemical plasticizing of PAN by methyl methacrylate at the temperature (T_g, $T_{tg\delta max}$) the modulus of elasticity in shear is changed slightly. The cohesive energy density is also reduced slightly because of the increase of the molar and Van der Waals volume of structural units.

In PBMA radicals of large size decrease significantly the density and create significant V_{mol} and $V_{w,}$ and thus create a considerable amount of free volume for the polymer chain mobility. Cohesion energy density is also reduced significantly (See Table 4).

Adding structural units in PBMA and PAN reduces significantly the temperature (T_g, $T_{tg\delta\ max}$), dielectric ε and tgδ_{max} parameters, density, elastic modulus value in shear and thus all these cause a significant effect on chemical plasticizing of PAN.

In Figure 1 it is shown the temperature dependence of the dielectric loss tangent for PBMA and for its copolymers with PAN. It can be seen that the chemical plasticizing of PAN by structural units of PBMA is presented by the decrease of $T_{tg\delta\ max}$ and by the changes in maximum

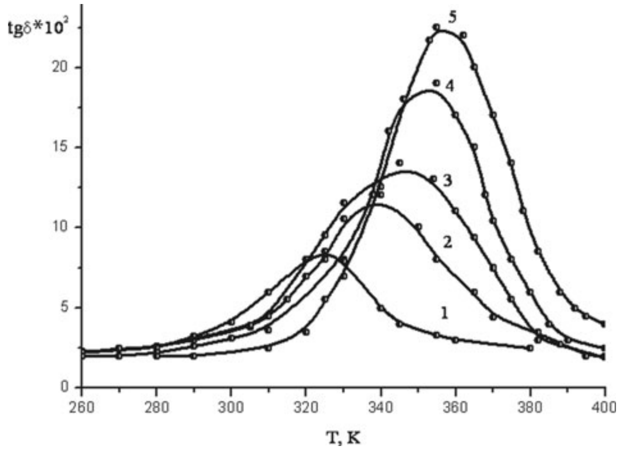

Figure 1. Temperature dependence of tg δ for films: PBMA (1) and copolymers AN – BMA; monomer ratio are 1: 3 (2), 1: 2 (3), 1: 1 (4), 2: 1 (5).

intensity of dielectric losses; this intensity decreases during the increase of content of structural units in PBMA copolymer.

Relaxation losses are caused by the processes of dipole polarization installation and due to the orientation of polar segments of macromolecules. They arise due to the overcome of internal friction forces (viscosity). The viscosity of the amorphous polymer in the glassy state is mainly determined by the free volume; the segmental mobility process develops due to the achievement of universal level of free volume for polymers of different composition and structure [2].

The universal value of free volume is higher for that polymer, which in the glassy state has a larger free volume below the T_g. By this it can be explained not only the bigger efficiency of structural units of PBMA rather than PMMA structural units efficiency in PAN, but also the significant decrease of T_g, $T_{tg\delta\ max}$ and the decrease of the intensity of the peak dissipation factor with increasing content of structural units PBMA in AN-BMA copolymer. By increasing the free volume the mobility of dipoles facilitates; forces of internal friction are added easier and thus the loss of power is reduced.

Figure 2 shows the temperature dependence tg δ for acrylonitrile copolymers with other monomers in the ratio 1:1. In AN-St copolymer the low tg δ intensity is caused by the decrease in polarity, by the reduction of the number of dipoles in the segments of PAN macromolecules chain. The comparison of AN-BA and AN-VB copolymers shows that the same value of dipole moment of structural units, the density of the last copolymer is lower than the AN-VB copolymer density. So the free volume of AN-VB copolymer is higher and it decreases the power loss during the electrical field effect (intensity of maximum dielectric loss angle is less). However, the chain stiffness of AN-VB copolymer is higher than in the AN-VA copolymer; that is why the development of segmental mobility is realized at higher temperature. The comparison of copolymers AN-MA and AN-BMA of the same structural units ratio shows the crucial role of intermolecular interactions in the intensity of the peak dissipation factor.

In AN-BMA copolymer the density is smaller and therefore the higher free volume value, which facilitates overcoming of internal friction forces. However, much larger values of cohesion energy and molar attraction constants indicate significant internal friction (viscosity); these cause higher tg δ_{max} intensity. The comparison of tg δ_{max} of AN-VBE and AN-BMA copolymers shows a lower intensity peak in AN-VBE copolymer. This is due to smaller forces

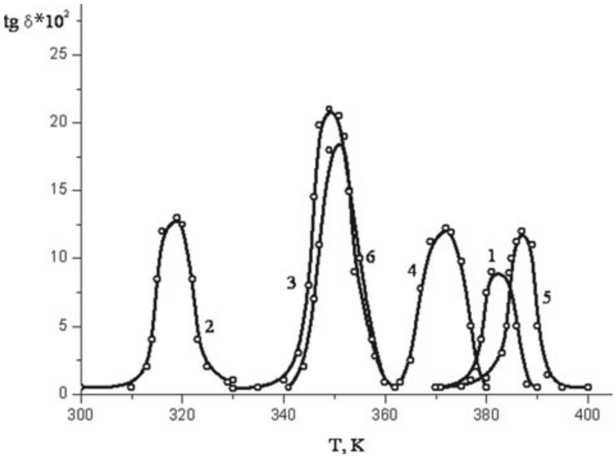

Figure 2. The temperature dependence of the dielectric loss tangent in polymers: AN-S (1), AN-VBE (2), AN-VA (3), AN-VB (4), AN-MMA (5), AN-BMA (6); the component ratio is 1: 1.

of attraction between macromolecules (this copolymer has lower values of μ_{ef}, E_{coh} e_{coh}). In addition, the density of copolymer is lower comparing with AN-BMA. This creates better conditions for polarization processes.

Partial replacement of structural units with side -CN polar groups (PAN) in the macromolecule chain into the non-polar styrene unit (copolymer AN-St) and also the partial replacement of side groups of PAN structural units with polar groups with lower or higher dipole moment, but those that increase the level of free polymer volume (copolymers AN-VA, AN-VBE, AN-VB and AN-BMA), comply with certain criteria for the T_g reduction and the decrease of other parameters values ($T_{tg\delta\ max}$, G_a).

In these copolymers plasticizing effect of chemical stiff-chain PAN is achieved by relaxing intra- and intermolecular interactions that decrease with the increase of polymer free. Therefore, for the above mentioned chemical PAN plasticizing the specific free volume (V_f) of the polymer system is crucial. V_f is proportional to the specific volume of the polymer, and the last is proportional to the molar volume of the polymer that is referred to the structural

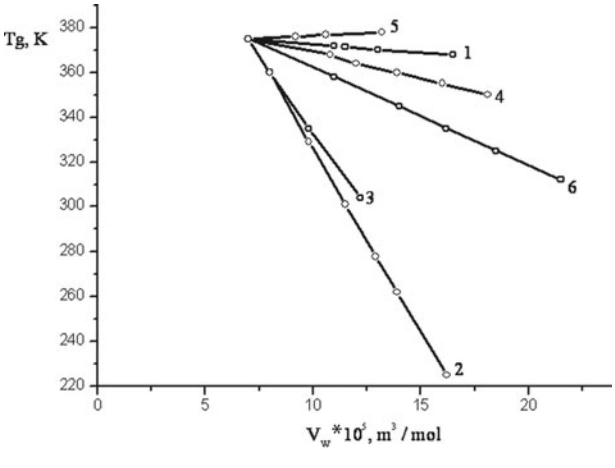

Figure 3. The dependence of T_g on the Van der Waals volume level during the chemical plasticizing of PAN by styrene (1) butyl vinyl ether (2), vinyl acetate (3), vinyl benzoate (4), methyl methacrylate (5), butyl methacrylate (6)

unit and Van der Waals volume (V_w) of this unit. Van der Waals volume is a space occupying unit, in which other units with energy that corresponds to normal temperature value can not penetrate.

According to Figure 3 T_g of PAN during the introduction into its chain the structural units of styrene, butyl vinyl ether, methyl- and butyl methacrylate, vinyl acetate, vinyl benzoate correlates with the Van der Waals volume of structural units.

Criteria for the T_g reduction of the polymer in case of this type of polymer chemical plasticization can be written down according to the following formula:

$$\Delta T_g = \text{const}\ \Delta V_w$$

Conclusions

Thus, the chemical plasticizing of stiff chain polymer PAN with different lateral polar groups comply certain rules. These rules apply to chemical plasticization of stiff chain polymer in case of partial replacement of structural units with polar side groups by nonpolar side groups. On the other hand, introduction of structural units with lateral polar groups into the chain can also increase the free volume of polymer due to their considerable size. The last facilitates the segments mobility and the reduction of T_g. Moreover, it is possible to cause the chemical plasticization by decreasing the cohesive energy density (in the case of copolymer AN-VA).

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