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Synthesis and CO_2 sorption in poly(1-trimethylsilyl-1-propyne) and polyvinyltrimethylsilane containing ethylene oxide groups and N-butylimidazol-based "ionic liquids" groups

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ABSTRACT

There have been developed methods of chemical modification of high permeable glassy polisilicon hydrocarbons poly(1-trimethylsilyl-1-propyne) [PTMSP] and polyvinyltrimethylsilane [PVTMS] for introducing into polymer structure of ethylene oxide groups and "ionic liquid-like" groups which are known as a group possessing strong CO_2 affinity. In addition low molecular compounds having structures close to chemically modified polymers have been synthesized in order to create mechanical blends with polymers. Sorption properties of modified polymers and mechanical blends were studied in order to establish influence of nature and quantity of introduced functional groups and also method of introducing of functional groups in PTMSP and PVTMS (chemical modification or preparation of mechanical blends) on ability of reversible interaction with CO_2. It was established that it is possible to surpass level of CO_2 sorption that is typical for initial PTMSP and PVTMS by introducing groups specific to CO_2, and, moreover, the level of sorption in such materials essentially depends on method of introducing of functional moieties.

Keywords: Carbon dioxide sorption; Polyacetylenes; Chemical modification; Ionic liquids; Poly(ethylene glycol)

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1. Introduction

Purifying of energy carriers methane and hydrogen from CO_2 as well as CO_2 recovery from mixtures with other gases is a challenging problem for the moment [1,2]. Furthermore, development of economically viable CO_2 capture processes is becoming increasingly important as concerns about greenhouse gas emission continue to receive worldwide attention [3]. Gas separation by membranes is highly desirable since separation by membranes is generally a low energy process. A large number of polymers membranes have been studied for CO_2/N_2, CO_2/H_2 separation [4]. It is known that glassy polysilicon hydrocarbons–poly(1-trimethylsilyl-1-propyne) [PTMSP] and polyvinyltrimethylsilane [PVTMS] have high CO_2 permeability [5,6]. However, selectivity of CO_2 recovery from mixtures of CO_2 with N_2, H_2 or CH_4 is insufficiently high. Therefore, it is of great interest to introduce in polymers groups which are capable for specific interaction with CO_2 in order to create materials with high separation selectivity of CO_2-containing gas mixtures.

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2. Material and methods

Creation of reaction centres is necessary for introducing groups which may provide high separation selectivity for CO_2-containing gas mixtures. Bromine groups can be one of such centres. It was established earlier that bromination of PTMSP and PVTMS is going to methyl group at silicon with formation following structure $(CH_3)_2$- Si-CH_{x-1} Br_x, where x = 1–3 and the maximum content of Br in obtaining product 30% wt. Br (in the case of PTMSP) and 60% wt. Br (in the case of PVTMS) [7,8]. Ethylene oxide groups and "ionic liquids" groups on the basis of quaternized N-butylimidazol have been chosen as groups which are capable to specific interaction with $CO_{2.}$ Two ways of preparation of membrane materials on the basis of polysilicon hydrocarbons were taken into consideration in order to establish the influence of the nature and quantity of functional groups as well as the method of introducing groups in PVTMS and PTMSP on ability to reversible interaction with CO_2. First method is two-stage chemical modification of PTMSP and PVTMS including synthesis of brominated polymer and subsequent polymer analogous reactions between reactive bromine group with low molecular poly(ethylene glycol) methyl ether (PEGME) to introduce ethylene oxide groups in polymer and with N-butylimidazol and subsequent anion-exchange reaction to introduce "ionic liquids" moieties. The second method is preparation of mechanical blends of PTMSP and PVTMS with low molecular compounds on the basis of products of interacting between halogen-containing compounds that have structure like brominated fragment in PTMSP and PVTMS - chloromethyltrimethylsilane (CMTMS) with PEGME and with N-butylimidazol.

2.1. Introducing of ethylenoxide groups

Bromine-containing PTMSP and PVTMS which were used for further modification were synthesized by method which was developed by our group and reported in [7,8].

The reaction scheme for PTMSP as an example is shown on Fig. 1. Reaction of bromine-containing polymer with low molecular PEGME was carried out in presence of metal sodium under argon atmosphere and at temperature +25°C. THF was chosen as a solvent of reaction and duration of experiment was 24 h.

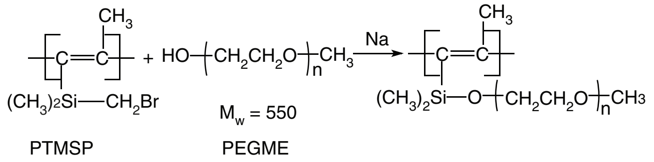


Fig. 1. Scheme of chemical modification of PTMSP by ethylene oxide groups.

Yield of reaction was calculated using elemental analysis data and it was established the yield up to 90% on brominated units. Taking into account the degree of bromination (maximum 27% wt. for PTMSP) it is possible to introduce in polymer structure up to 60% wt. of PEG.

The structure of reaction product was confirmed by IR-spectroscopy (Fig. 2).

As one can see from Fig. 2 the IR-spectrum of (PTMSP-PEG) product in comparison with initial brominated polymer demonstrates the appearance of new intensive bands corresponding to vibrations of a C-O-C bond (950–1100 sm^{-1}) and at the same time disappearance of a band at 580 sm^{-1} corresponding to vibrations of a C-Br bond.

Polymer samples of PTMSP and PVTMS with the grafted ethylene oxide groups were synthesized by above-described method. The content of groups in polymers was calculated using elemental analysis data (Table 1). The synthesized samples—PTMSP-PEG20, PTMSP-PEG50, PVTMS-PEG45—contain 20, 50 and 45% wt. of PEG groups respectively.

2.2. Introducing of "ionic liquid" groups

Introducing of ionic liquid-like groups was carried out in two stages. As an example the reaction scheme for PVTMS is shown on Figs. 3a,b. The first stage is quaternization of N-butylimidazol by bromine-containing polymer (Fig. 3a). Reaction was carried out under argon atmosphere and at temperature +25°C,

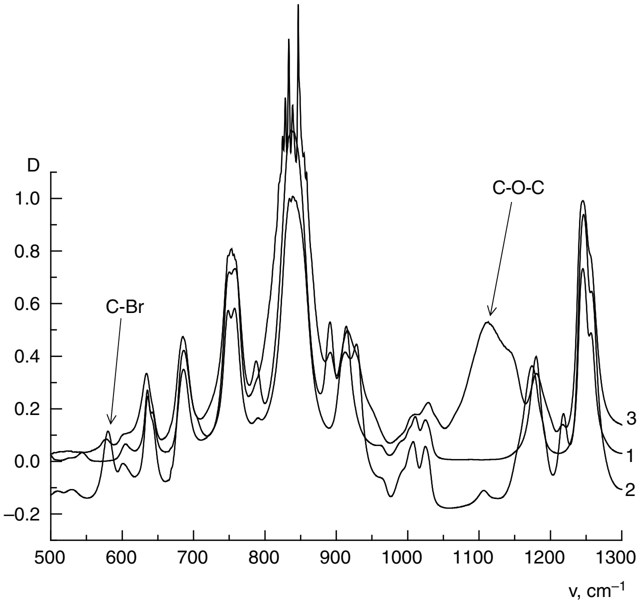


Fig. 2. IR-spectrums: 1 – PTMSP, 2 – Br-PTMSP, 3 – product of reaction (PTMSP-PEG).

Table 1
Elemental analysis data bromine-containing polymers and samples after modification by PEGME

	Elemental analysis data, % wt.									
	experimental					calculated				
	C	H	Si	Br	O	C	H	Si	Br	O
Br-PTMSP	51.05	9.40	19.55	20.00	0.00	–	–	–	–	–
PTMSP-PEG20	53.90	9.20	18.65	13.10	5.15	53.62	9.33	18.44	13.42	5.19
PTMSP-PEG50	55.00	8.80	16.05	7.00	13.15	55.08	8.82	16.01	7.12	12.97
Br-PVTMS	32.10	5.60	10.30	52.30	0.00	–	–	–	–	–
PVTMS-PEG45	34.00	4.95	10.15	35.70	15.20	34.17	5.11	10.14	35.55	15.03

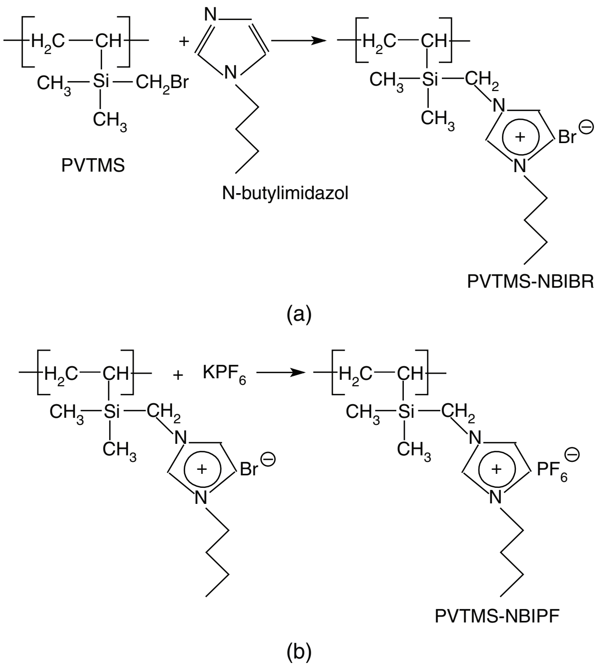


Fig. 3. Scheme of introducing of "ionic liquid like" groups into PVTMS structure.

CCl4 was chosen as a solvent, duration of experiment was 48 h. The maximum yield of reaction (according to the elemental analysis) on bromine unit is about 40% (in the case of PVTMS), 30% (in the case of PTMSP), that is about 28% wt. and 21.5% wt. of N-butylimidazol respectively. The second stage is anion-exchange reaction of obtained quaternized product with KPF6 (Fig. 3b). Reaction was carried out under argon atmosphere and temperature +25°C, mixture THF-acetone (ratio 4:1) was chosen as a solvent, duration of experiment was 48 h. The reaction yield is close to the quantitative according to the element analysis.

The structure of PVTMS-NBIBR product was confirmed by IR-spectroscopy (Fig. 4).

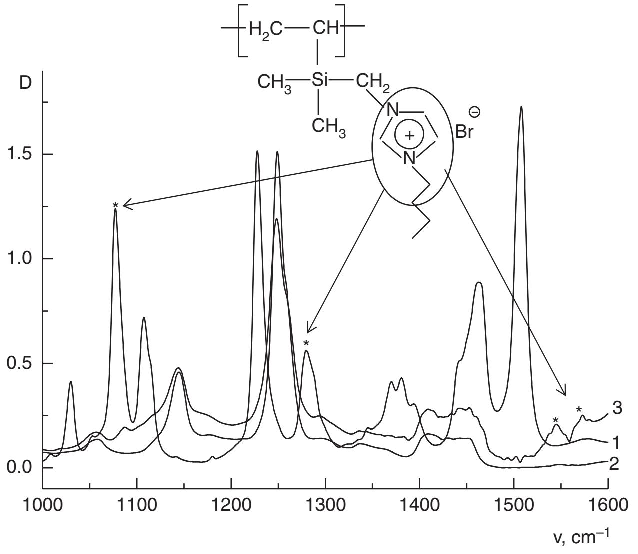


Fig. 4. IR-spectrums: 1 – n-butylimidazol; 2 – Br-PVTMS; 3 – product of reaction (PVTMS-NBIBR).

As one can see from Fig. 4 new intensive bands corresponding to N-butylimidazol appear in IR-spectrum of the product (PVTMS-NBIBR). These bands are shifted in comparison with a spectrum of initial N-butylmidazole. It is especially visible on bands of skeletal oscillation of aromatic cycle (1462, 1508 sm^{-1}) which are shifted towards short waves (1545 and 1573 sm^{-1}). This testifies that N-butylimidazol is not an admixture but it is chemically bonded with brominated polymer. As a result of such interaction the electronic density of aromatic cycle in imidazol is dislocated and that leads to such shifting of bands.

Polymer samples of PTMSP and PVTMS with quaternized imidazolium groups were synthesized by the above mentioned technique. The content of imidazolium groups in polymers was calculated using elemental analysis data (Table 2). The received samples—PTMSP-NBI20, PVTMS-NBI20—both contain 20% wt. of imidazolium groups.

Table 2
Elemental analysis data of bromine-containing polymers and samples after modification by N-BI

	Elemental analysis data, % wt.									
	experimental					calculated				
	C	H	Si	Br	N	C	H	Si	Br	N
Br-PTMSP	51.05	9.40	19.55	20.00	0.00	–	–	–	–	–
PTMSP-NBIBR20	53.05	9.55	18.90	15.55	2.95	53.02	9.58	18.78	15.47	3.15
Br-PVTMS	32.10	5.60	10.30	52.30	0.00	–	–	–	–	–
PVTMS-NBIBR20	36.55	5.70	8.95	45.75	3.05	36.52	5.73	8.96	45.84	2.95

Then the anion-exchange reaction was carried out on received quaternized polymers according to the scheme (Fig. 3b). Identification of products of the anion-exchange reaction was performed by elemental analysis because the IR-spectroscopy doesn't fix ionic bonds. Elemental analysis data have shown absence of Br in the samples obtained in the result of the anion-exchange reaction.

2.3. Synthesis of low molecular modeling compounds for preparation of mechanical mixtures

Low molecular modeling compounds M-PEG and M-PF on the basis of CMTMS having structure like brominated fragment in PTMSP and PVTMS were synthesized in order to create better compatibility of mechanical blends with polymers.

The schemes of synthesis of models M-PEG is represented on Fig. 5. Reaction was carried out under argon atmosphere and at temperature + 25°C, THF was chosen as a solvent and duration of reaction was 24 h. The yield of reaction was up to 90% (calculated using elemental analysis data).

The schemes of synthesis of models M-PF is represented on Figs. 6a,b. The first stage of reaction was carried out under argon atmosphere and at temperature of reaction + 45°C, THF was chosen as a solvent and duration of reaction was 12 h. The yield of reaction on halogen is about 90% according to the elemental analysis. The temperature of second stage was +25°C, acetone was chosen as a solvent and duration of reaction was 48 h. The yield of second stage is close to the quantitative according to the elemental analysis.

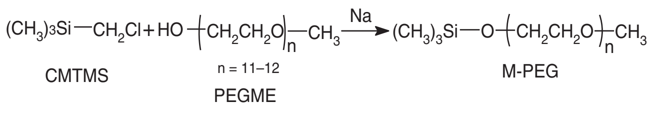
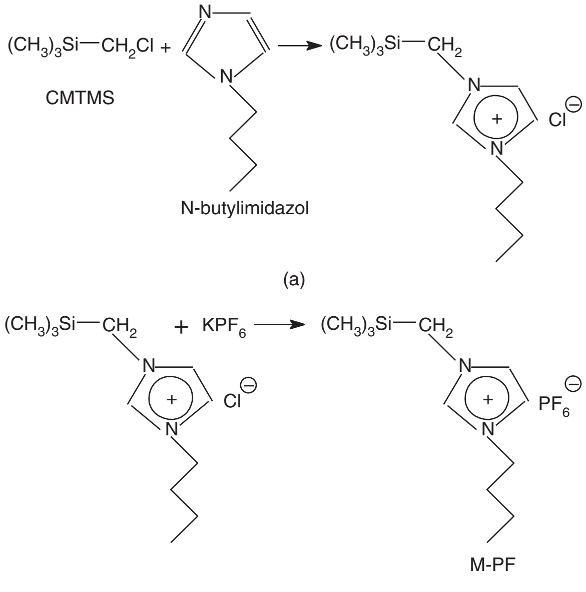


Fig. 5. Scheme of M-PEG model synthesis.



(a)

(b)

Fig. 6. Scheme of M-PF model synthesis.

3. Investigation of CO_2 sorption

CO_2 sorption of the obtained blends and the modified polymers was studied in order to establish the influence of the nature and quantity of functional groups as well as a method of introducing of groups in PVTMS and PTMSP (chemical modification or preparation of mechanical blends) on ability to reversible interaction with CO_2. Sorption was studied on films prepared from mechanical blends of polymers with the low-molecular models by casting from solution in chlorobenzene or toluene on cellophane as well as on powders of initial and chemically modified polymers. Blends of polymers (both PTMSP and PVTMS) with models, containing 20 and 50% wt. of M-PF as well as chemically modified samples of PTMSP and PVTMS with «ionic liquids» groups, containing 20% wt. of N-butylimidazol were investigated. CO_2 sorption for mixtures of PTMSP and PVTMS with another model containing 20 and 50% wt. M-PEG and for chemically modified polymers by PEGME (20 and 50% wt. PEG) was also investigated.

CO_2 sorption was measured on setup "Magnetic suspension balances, (MSB) Rubotherm" in the temperature range 0–35°C and in pressure range 3–10 bar. The system thermostated at temperature that is needed and the sample is pumped out under vacuum to constant weight. After this, CO_2 was delivered into the system at given pressure. The weight of the sample starts to increase that is registered on the electronic display of microbalance. On the equilibrium sorption achievement the increasing of the sample weight stops. At this stage of polymer saturation with CO_2, the weight reading from the microbalance is recorded as S_{MP}.

The absorbed amount of gas is calculated using the following equation:

$$m_{\text{abs}} = S_{MP} + \rho_{\text{gas}}\left[V_{r-b} + V_p + V_{sw}\right] - m_{\text{vac}}$$

where ρ_{gas} is the density of the gas calculated from a state-equation (with known pressure and temperature), V_{r-b} and V_p are the volumes of the rod-basket assembly and of the original polymer, respectively, and V_{sw} is the increase of the original sample volume due to swelling. The term $\rho_{\text{gas}} \cdot [V_{r-b} + V_p + V_{sw}]$ represents the buoyancy force.

The volume of the road-basket assembly is determined from buoyancy experiment, when no sample is charged into basket:

$$0 = S_{MP} + \rho_{\text{gas}}V_{r-b} - m_{\text{vac}}$$

The volume of the rod-basket assembly is determined by estimating the density of the gas and measuring the weights, S_{MP} and $m_{\text{vac.}}$

From the Fig. 7 it is visible that level of CO_2 sorption of PTMSP goes down at addition of 20% wt. of M-PF model, possibly because of reduction of free volume of polymer and therefore reduction of CO_2 sorption in free volume elements, however the mixture with 50% wt. shows higher CO_2 sorption level in comparison with a blend containing 20% wt of M-PF. Such CO_2 sorption increase with increase of low-molecular «ionic liquid» is a result of sorption due to solubility of CO_2 in low-molecular « ionic liquid», however it is not possible to exceed the CO_2 sorption level of pure PTMSP. In the case of chemically modified PTMSP (PTMSP-NBIPF6) CO_2 sorption is essentially higher in comparison with blends and even initial PTMSP.

In case of PVTMS, CO_2 sorption is higher than sorption in pure PVTMS even at addition of 20% wt. of and increases further at addition of 50% wt. (Fig. 8).

Such differences in behavior of blends both PTMSP and PVTMS are due to differences in free volume of these polymers. PTMSP has bigger free volume in comparison with PVTMS: fraction of free volume is 31% in PTMSP and 21% in PVTMS [9]. The basic contribution in CO_2 sorption of high-permeable PTMSP brings the sorption in free volume elements, therefore the level of sorption in mechanical blends falls, unlike PVTMS having much smaller free volume.

The other reason of differences in sorption is inequality between CO_2 sorption levels of model and of polymers (Fig. 9). CO_2 sorption level of PTMSP is essentially

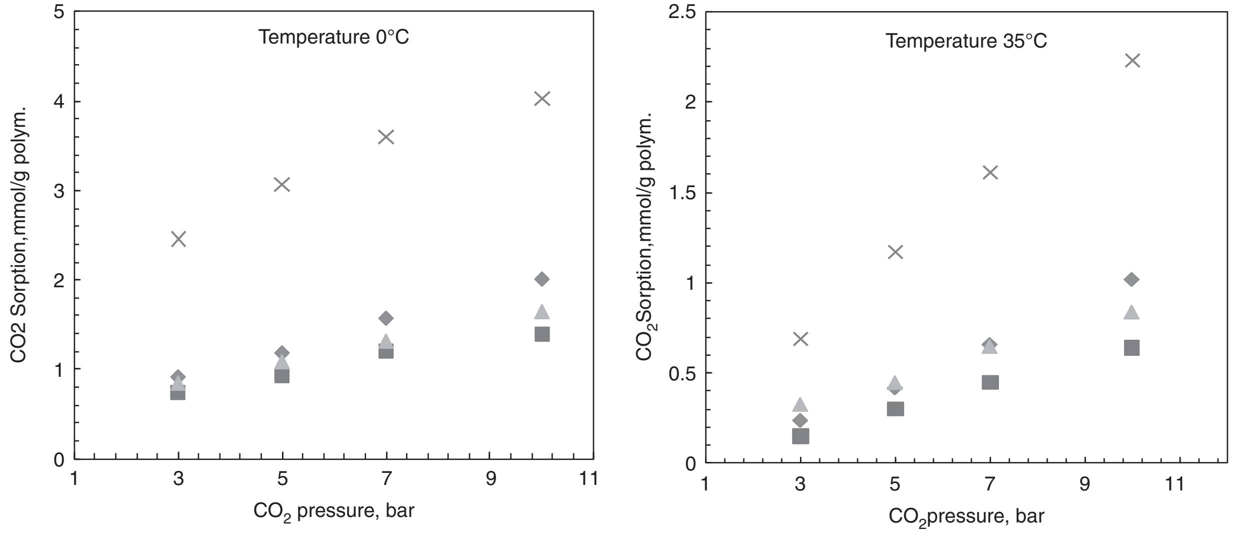


Fig. 7. Data of CO_2 sorption in PTMSP with "ionic liquids" (chemically modified and mechanical blends): ◊ – PTMSP, ☐ – PTMSP + 20% wt. M-PF, Δ – PTMSP + 50% wt. M-PF, × – PTMSP-NBIPF20.

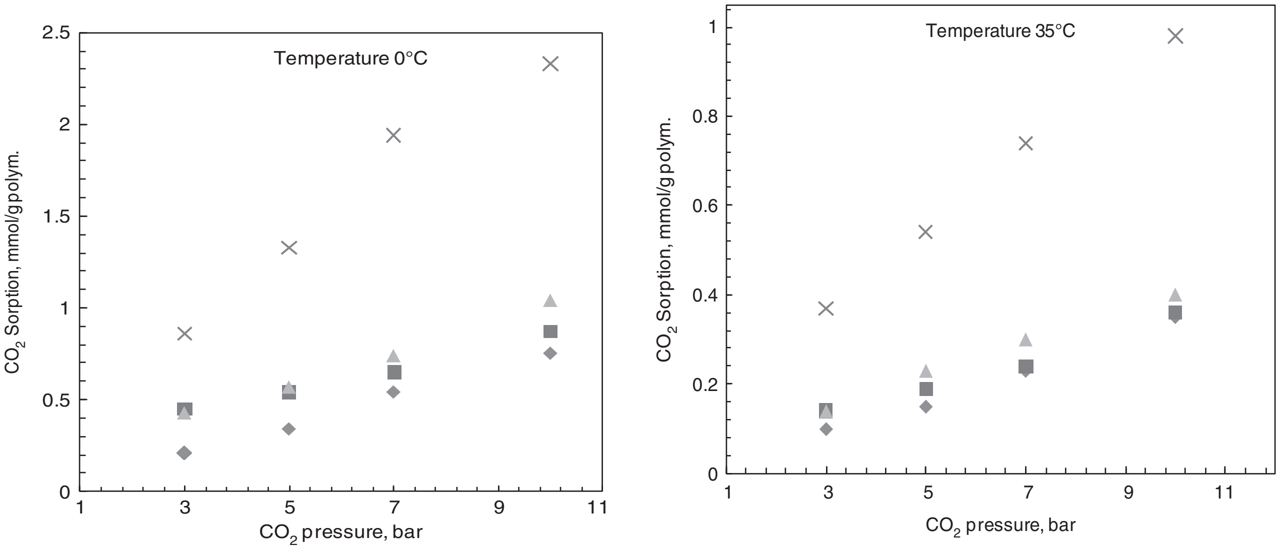


Fig. 8. Data of CO_2 sorption in PVTMS with “ionic liquids” (chemically modified and mechanical blends): ◊ – PVTMS, □ – PVTMS + 20% wt. M-PF, Δ – PVTMS + 50% wt. M-PF, × – PVTMS-NBIPF20.

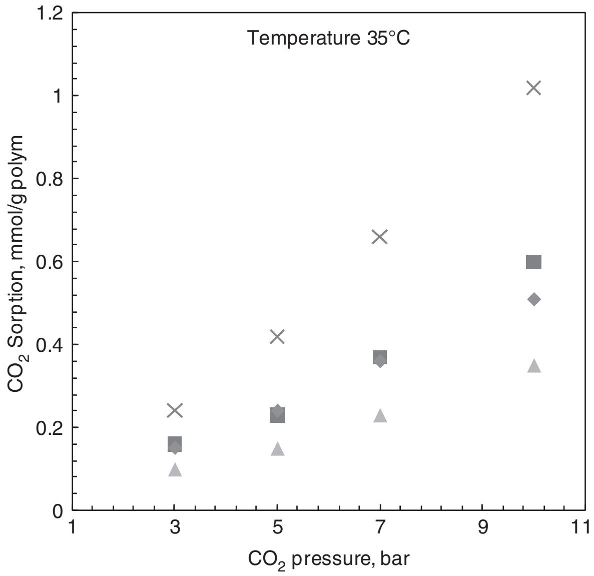


Fig. 9. Comparison of CO_2 sorption data in polymers and models: ◊ – M-PEG, □ – M-PF, Δ – PVTMS, × – PTMSP.

higher then CO_2 sorption level of model M-PF, therefore in the case of PTMSP-PF blends it is impossible to surpass the sorption level of initial PTMSP. On the contrary, CO_2 sorption level of PVTMS is lower in comparison with CO_2 sorption level of M-PF and it is possible to increase sorption level by adding of model M-PF to PVTMS. As has been studied, CO_2 sorption in PVTMS-NBIPF20 (chemically modified by N-butilimidazol, content of N-butilimidazol in polymer is 20%wt.) the level of CO_2 sorption in chemically modified PVTMS also essentially higher than in pure PVTMS.

CO_2 sorption of PTMSP decreases at addition of 20% wt. of M-PEG, and continues to decrease further at addition of 50% wt. according the data from Fig. 10. CO_2 sorption in PTMSP chemically modified by PEGME is higher than in mechanical blends, but not so considerable as in the case of “ionic liquids”.

As it was marked previously, high sorption ability of PTMSP is caused mainly by high free volume of polymer and as a consequence high sorption in free volume elements. The reason of decreasing of CO_2 sorption in PTMSP+M-PEG blends, as well as in blends with M-PF are differences in sorption levels of PTMSP and M-PEG models (see Fig. 9). However, it is visible from the figure that decrease of sorption in PTMSP blend with M-PEG is more considerable in comparison with the decrease of sorption in PTMSP blend with M-PF (see Fig. 7). Taking into consideration the fact that the levels of sorption of the models M-PEG and M-PF are close to each other (see Fig. 9), this decrease of sorption in the case of PTMSP blend with M-PEG is possibly connected with the fact that more high-molecular M-PEG model is worse compatible with a polymeric matrix and distributed mainly in free volume elements whereas M-PF model has better miscibility with PTMSP matrix and improves sorption properties of a continuous phase.

In case of PVTMS the sorption levels of initial PVTMS and with added M-PEG model are virtually the same (Fig. 11). The reason of this fact is similar sorption levels of models M-PEG and initial PVTMS (see Fig. 9). Chemical modification of PVTMS by PEGME slightly decreases the sorption level in comparison with initial PVTMS, and that can be connected with the change of macromolecular chains packing influenced by long-chain ethylene oxide substituents in the side-chain which are capable to intermolecular interaction.

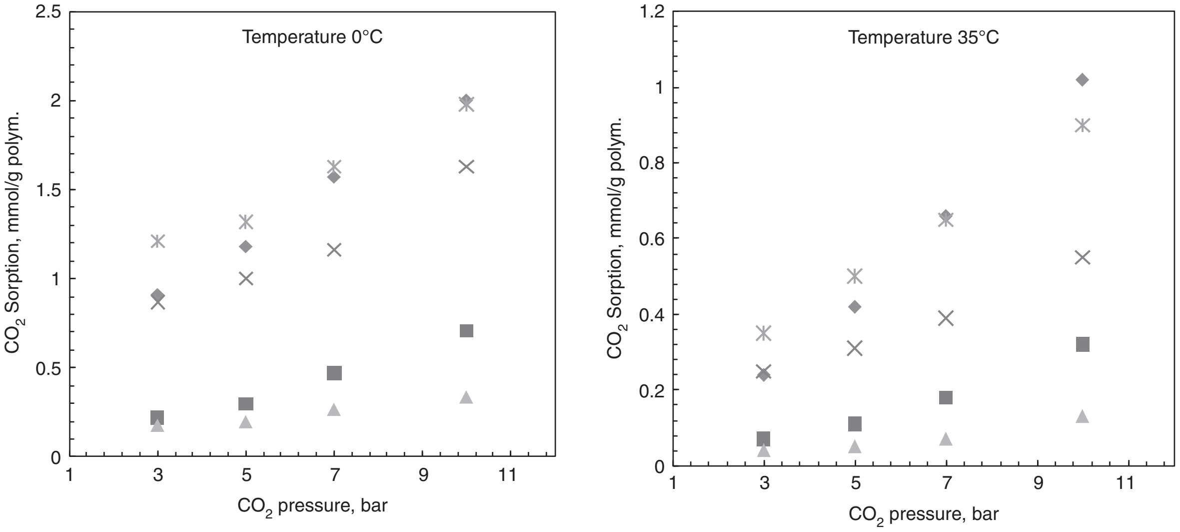


Fig. 10. Data of CO_2 sorption in PTMSP with ethylene oxide groups (chemically modified and mechanical blends): ◊ – PTMSP, □ – PTMSP + 20% wt. M-PEG, Δ – PTMSP + 50% wt. M-PEG, × – PTMSP-PEG20, ⋇– PTMSP-PEG50.

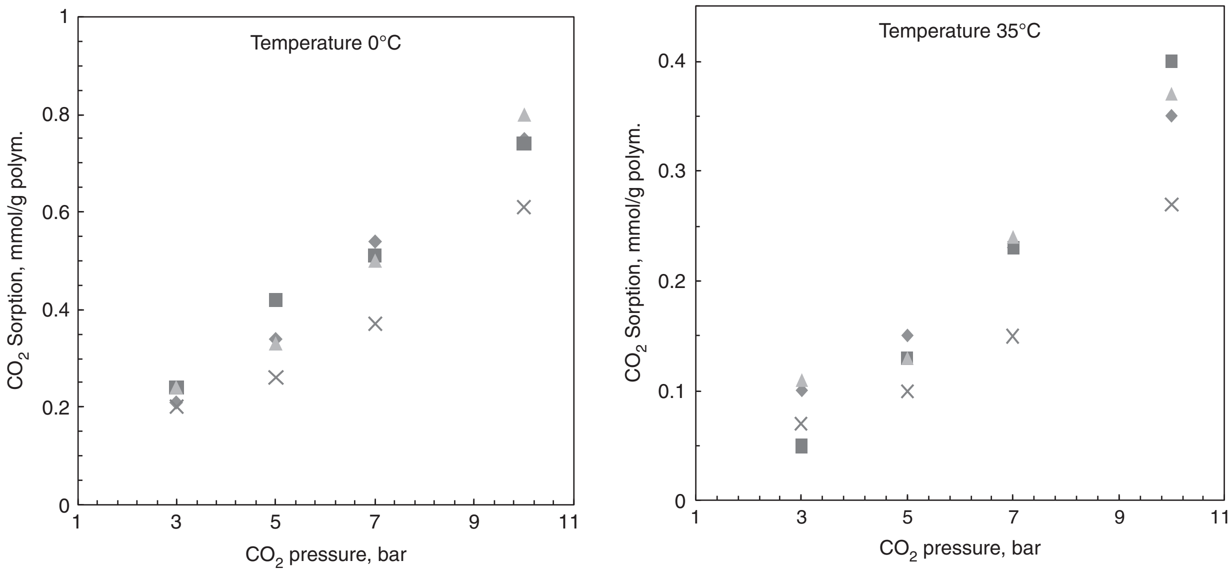


Fig. 11. Data of CO_2 sorption in PVTMS with ethylene oxide groups (chemically modified and mechanical blends): ◊ – PVTMS, □ – PVTMS+ 20% wt. M-PEG, Δ – PVTMS + 50% wt. M-PEG, × – PVTMS-PEG45.

4. Conclusions

The method of chemical modification of PTMSP and PVTMS for introducing into polymer structure of ethylene oxide groups and quaternized N-butylimidazol groups was developed. Also low molecular compounds having structures similar to fragments of halogenated polymers units have been synthesized in order to create mechanical blends with polymers. CO_2 sorption investigations established that it is possible to surpass level of CO_2 sorption that is typical for initial PTMSP and PVTMS by introducing groups specific to CO_2, and, moreover, the level of sorption in such materials essentially depends on method of introducing of functional moieties. Character of changes of sorption characteristics of chemically modified PTMSP and PVTMS and their blends is explained from the position of changes in free volume and differences in sorption levels of these polymers in comparison with added models. It was determined that CO_2 sorption in chemically modified polymers is basically higher than that in mechanical blends with similar mass composition. “Ionic liquids” have a greater influence on CO_2 sorption properties than ethylene oxide groups and that is true both for chemically modified polymers and mechanical blends.

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